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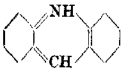
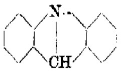
103 — *for* "" *read* ""

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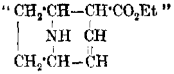
" *for* "

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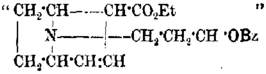
"

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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

he Conception of the Chemical Element as Enlarged by the Study of Radioactive Change.

A Lecture delivered before the Chemical Society on
December 19th, 1918.

By Frederick Soddy.

HE Council of the Chemical Society have honoured me with the nvitation to deliver one of three lectures bearing on the ultimate onstitution of matter, and I accepted the invitation in my desire o show how greatly I appreciated it rather than with any propect of being enabled, when the time came, to say anything on the subject which has not already been said before. The problem of the ultimate constitution of matter belongs to another world than that through which for the past four years we have been living, and although hostilities have at length ceased, and we may look forward to an opportunity of resuming in the future the thread of our philosophical investigations, philosophy herself is not so easily to be resumed. Novel in one sense as are the ideas introduced into the concepts of physics and chemistry by the study of radioactivity, four years' interruption has made them appear rather as a remote historical accomplishment than as a contemporaneous development. Although no longer new, however, the more as the subject matures does it become apparent that these advances are of fundamental and increasing importance to the chemist.

One would perhaps have expected that on the first and most fundamental conclusion arrived at in the study of radioactive change that the change is of a transmutational character, involving the spontaneous disintegration of the radio-element into others, it would have been the chemists who would have been most deeply interested, and who would have weighed the evidence and pronounced a decision. Yet judgment on the view, which was put forward more than fifteen years ago, on evidence in my opinion even then deserving of serious consideration, although accepted and universally adopted by the workers in the subject and by physicists, has gone by default so far as the majority of chemists are concerned. From the first, much of the most important evidence has been of a singularly simple and convincing chemical character.

The Transmutational Character of Radioactive Change.

If a chemist were to purify an element, say lead from silver, and found, on re-examining the lead at a later date, that silver was still present, and, again and again repeating the process, found always that silver, initially absent, reappeared, would he not be forced to conclude that lead was changing into silver and that silver was being produced by lead? It is because of the absence of evidence of this kind that the doctrine of the unchangeability of the elements has grown up. One positive example of the kind in question and that doctrine would be at an end. The conclusion to which in 1902 Sir Ernest Rutherford and I were forced with regard to the element thorium was based on evidence of this direct and simple nature. By simple purification, by chemical and physical means, constituents responsible for the greater part of the radioactivity of thorium can be separated, and as often as they are separated they are regenerated at a perfectly definite and regular rate. One of these constituents, the emanation, is gaseous, and it can be separated from the thorium by no more elaborate means than by a puff of air. Certainly the actual quantity of thorium emanation is infinitesimal, but this did not hinder its complete chemical characterisation, for it was found to pass unabsorbed through every reagent tried, one or other of which would have absorbed every known gas with the exception of the gases of the argon family. The conclusion that the thorium emanation was a gas of the argon family produced by thorium, later extended to the similar gaseous products of radium and actinium, was a purely experimental conclusion reached before any theory whatever as to the nature of radioactivity had been advanced.

Another constituent responsible for part of the radioactivity we called thorium-*X*. It is left in the filtrate when a solution of thorium is precipitated with ammonia, although not when the thorium is precipitated by other reagents, such as sodium carbonate or phosphate. After this removal, however, thorium-*X* re-forms in the thorium. Moreover, it is thorium-*X*, not thorium, that produces the emanation. The latter in turn produces the non-volatile active deposit, in which the successive products, called thorium-*A*, -*B*, -*C*, and -*D*, are now recognised. The false interpretation of a similar phenomenon in the case of radium, before the radium emanation had been recognised, led to the view that inactive matter could be rendered temporarily radioactive by "induction," through contact with or association with radioactive matter. In the case of thorium, the discovery of the chemical character of the thorium emanation rendered the nature of the phenomenon clear almost from the first.

This, taken in conjunction with the atomic character of radioactivity, recognised by Mme. Curie from the start, and with the fact that the law of radioactive change proved to be the same as the law of unimolecular reaction, made the conclusion that the radio-elements were undergoing a series of successive changes, in which new elements are produced, of chemical and physical character totally distinct from those of the parent element, the only one capable of explaining the facts.

Novel and unexpected as it was to find transmutation spontaneously in progress among the radio-elements, the phenomena this explanation explained were equally novel and transcended what to a generation ago would have appeared to be the limits of the physically possible.

It is to pay chemistry a poor compliment to represent this conclusion as in any way contrary to the established foundations of chemistry. If it had not been for the correct conception of the nature of chemical change, the clear distinction between atoms and molecules, and the conclusion that in all changes in matter hitherto studied the element and the atom of the element remain essentially unchanged, which we owe to the founders of chemistry, the character of radioactivity would not have been arrived at so quickly. On the other hand, if radioactivity had not been almost instantly recognised as a case of spontaneous transmutation, then, if you will, there would have been something radically wrong with chemistry and the training it affords in the elucidation of the metamorphoses of matter.

With regard, however, to the various claims that have been made since that transmutational changes can be artificially effected, by the aid of the electric discharge in gases or the rays from radium, I have always regarded the evidence in this field as capable of simple alternative explanation. Different investigators have obtained entirely opposite results, and there is not that consensus of evidence one finds among those who have investigated radioactive change.

In another direction there has been a tendency to underrate the unique and unparalleled phenomenon of radioactive change, and to connect what is entirely and solely a development of the new experimental science of radioactivity, with the somewhat older isolation of the electron and the electronic hypotheses of the constitution of matter to which that discovery have given rise. For example, Sir J. J. Thomson in his Romanes Lecture, 1914, says: "Since the electron can be got from all the chemical elements we may conclude that electrons are a constituent of all the atoms. We have thus made the first step towards a knowledge of the structure of the atom and towards the goal towards which since the time of Prout many chemists have been striving, the proof that the atoms of the chemical elements are all built up of simpler atoms—primordial atoms, as they have been called." The removal of electrons from matter occurs in physical, chemical, and radioactive changes alike, exampled, respectively, by the electrification of a glass rod by friction, the ionisation of an electrolyte by solution, and by the β-ray change of radioactive substances. It is only in the latter case, however, that the electron can be regarded as a primordial constituent and the change as transmutational. Even to-day it is in radioactive phenomena, and in these alone, that the limits reached long ago in the chemical analysis of matter have been overstepped and the Rubicon, which a century ago Prout vaulted over so lightly in imagination, has actually been crossed by science.

First and Second Phases of Development.

Looking backward to the first recognition of the character of radioactive change in 1902, it is possible to distinguish broadly two phases. The first phase, concerned mainly with the disentanglement of the long and complicated series of successive changes, commencing with the two primary radio-elements uranium and thorium, and including ultimately all the known radio-elements, added little to the conceptions of chemistry beyond the disturbing fact that the radio-elements, although in every other respect analogous to the ordinary elements, are in process of continuous transmutation. But in the second and more recent phase of radioactive change, the study of the chemical character of the successive products and the law connecting this with the type of ray expelled in the change, the discovery of elements with different radioactive but identical chemical character, the recognition of these as isotopes, or elements occupying the same place in the periodic table, and the interpretation of the significance of the periodic law, conceptions are arrived at which are not merely novel, but upsetting. In this phase, an aspect of the ultimate constitution of matter has been revealed that, although well within the scope of the conceptions of elements and atoms which we owe to the nineteenth century, nevertheless has totally escaped recognition. I am not much concerned with definitions, but I think the Chemical Society might safely offer a prize of a million pounds to any one of its members who will shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of a first-year student of chemistry at the present time.

Chief Features of Radioactive Change.

The features that distinguish radioactive change from chemical change, and which have made it possible in a few short years to reduce to some degree of finality and completeness the intensely complicated series of successive changes suffered by the elements uranium and thorium in the course of their disintegration, are chiefly two. In the first place, the whole phenomena are inevitable, incapable of being changed or deviated from their allotted course by any means whatever, independent of temperature, concentration, or the accumulation of products of reaction, the presence of catalysts, irreversible and capable of being accurately and quantitatively followed without alteration or disturbance of the changing system. The mathematical theory, although for many successive changes it becomes cumbrous and unwieldy to a degree, involves only the solution of one differential equation by a device quite within the compass of anyone possessing a knowledge of the bare elements of the calculus to employ. The second feature is in the magnitude of the energy evolved, which, weight for weight of matter changing, surpasses that evolved in the most exothermic chemical changes known, from one hundred thousand to a million times. Manifested in the form of rays, by their fluorescent, photographic, or ionising power capable of being put into evidence in almost inconceivably minute amount, changes are capable of being followed, and by the electroscope accurately measured, which would conceivably require to continue for millions of years before they could be experimentally detected by chemical or even by spectroscopic methods. The disintegration of the single atom is ascertainable, for example, in the spinthariscope of Sir William Crookes, where each of the scintillations separately visible is due to the impact of a single α-particle on the zinc sulphide screen. On the same principle, methods have been developed and are in regular use for counting the number of atoms disintegrating per minute, whereas to the spectroscope at least $3 \cdot 10^{13}$ atoms as a minimum must be present, 25,000 times as many atoms as there are human beings alive in the world, before any element can be so detected. By the most curious compensation, almost of the nature of a providential dispensation which some may have found difficult to believe, the quantity of matter of itself is not of importance in investigating radioactive change. The methods depend on the rate of emission of energy, and this is proportional to the quantity of the changing element multiplied by its rate of change. In the disintegration series, the various members accumulate in quantities inversely proportional to the rates of change, and so it comes about that all changes within the series are equally within the scope of the method whether, as in the case of the parent elements, they involve periods surpassing the most liberal estimates of the duration of geological time or, as in the case of the C' members, are estimated to run their course in a time so short that light itself can travel but a very few millimetres, before the next change overtakes the changing atom.

The condition of radioactive equilibrium in which the quantities of the successive products assume the above stationary ratio is of course entirely different from chemical equilibrium, and is the condition in which for each member of the series except the first as much is produced as changes further in the unit of time.

The foregoing applies so long as the changes continue. When they are finished and it is a question of ascertaining the ultimate products, the task may be likened to that of searching for a meteor which a moment before lit up the heavens and now has vanished into the night.

The Ultimate Products.

It is a matter for surprise that in all radioactive changes so far studied there appear to be only two ultimate products, helium and lead, the former constituting the α-particles and the latter being produced both by uranium and thorium, withal, as we now know, not the same lead in the two cases. There are sufficient experimental reasons for doubting whether the disintegration of an atom into more nearly equal parts would be within range of detection by any of the known methods. A heavy atom like oxygen, for example, if expelled as a radiant particle, might not attain sufficient velocity to ionise gases, or, even if it did, the range over which the ionisation would extend, as we know from the ionisation produced by the recoil atoms, would be extremely small. It must be a matter for comment, however, that hydrogen never appears in these changes, as, if it were produced, it would almost certainly be as easy to ascertain as helium. It has always seemed to me a possibility that some genetic connexion may exist, after all, between thorium and uranium, although I have never been able to frame even a possible mode of so connecting these two elements. With a difference of atomic weight of six units, it is impossible to pass from one to the other by addition or expulsion of helium atoms alone.

Both with regard to helium and lead, the composition of radioactive minerals gave the first clue to the identity of the ultimate products. After the discovery of radioactivity and the elucidation of its nature, the fact that helium was found only in minerals containing uranium and thorium assumed a totally new interpretation, borne out by the spectroscopic proof of the production of helium from radium by Sir William Ramsay and myself, and later from actinium, polonium, and even from uranium and thorium, all at the rates to be expected from radioactive data. The identification of the α-particle with helium, after the weight of the α-particle had been shown by new physical methods to be four times that of the hydrogen atom, was accomplished by enclosing the radium emanation in a glass tube thin-walled enough to allow the α-particle to go through, but perfectly impervious to the passage of gas. In these circumstances, helium in spectroscopically detectable quantity was proved by Rutherford to make its appearance outside the tube.

Such confirmations by the spectroscope, welcome and gratifying as they are, are nevertheless in a sense subsidiary to the main problem, namely, the task of unravelling the complicated series of changes into its individual steps, and the characterisation by their radioactivity of the several intermediate members of the series, such as by the determination of their periods and the physical constants of the radiation α-, β-, or γ-, to which they give rise. The determination of their chemical character, although equally important, was only later fully accomplished.

The Radiations.

In the successive radioactive changes, α- or β-particles are expelled, one α-particle per atom disintegrating for each change, although for the β-particles our knowledge is less exact. In some cases, certainly, although these are exceptional, β-particles seem to be expelled along with α-particles. The α-particle is an atom of helium charged with two atomic charges of positive electricity, or, as we should now say, is the helium nucleus, deprived of the two electrons which are combined with it in the helium atom. The β-particle is the negative electron, and when expelled with sufficiently high velocity is accompanied with γ-rays. The latter are *X*-rays of exceedingly short wave-length, varying from 1·3 to 0·1 Ångström units.* A connexion exists between the speed of the change and the speed of the particles expelled, and the more rapid the change the faster in general and the more penetrating are the attendant α- or β-particles. In the case of the α-particle, an empirical logarithmic relation, known as the Geiger-Nuttall relation, enables us to calculate approximately the period of the changing element from the velocity or range of the α-particle, and vice versa, and by this means periods too long or too short to be directly measurable have been estimated. In the case of the β-rays, no definite quantitative law has yet been made out, but it is clear that a similar relationship must exist. One of the important corollaries is that changes much slower than the slowest known, namely, those of uranium and thorium, would probably not be detectable, as, even were α- or β-particles expelled, they would be of too low velocity probably to ionise gases or show fluorescent or photographic actions. Indeed, for mesothorium-*I* and actinium this appears to be the case. No detectable radiation is expelled, although the products conform to what would occur in β-ray changes. The period of both substances is long, and it is probable that the β-particle is expelled, but is undetectable by ionisation methods. For the slowest β-ray change, that of radium-*D*, with a period of twenty-four years, the β-radiation is of such low velocity as to be only capable of detection by special care, and is far less penetrating than average α-rays. These facts serve to show that changes may be going on in the non-radioactive elements which at present are beyond experimental means of detection.

Period of Average Life.

The law of radioactive change, which is the same for all cases, is that of unimolecular reaction, the rate of change, or quantity changing in unit of time, being a fraction, designated by λ and known as the radioactive constant, of the amount present. The value of λ, although vastly different for different radio-elements, is an absolute constant, so far as is known, for any one element, independent of every consideration whatever. The period of average life is the reciprocal of this constant, but the actual life of any one atom may assume any value. This is an experimental fact very difficult to account for. For example, it is quite easy to compare the value of λ for a collection of atoms (1) only just produced and not in existence a short interval before, and (2) that have remained undistinguished from an originally very much greater number, and each of which has been in existence many times the period of average life. In both cases the value of λ is the same. This fact excludes from consideration as a conceivable cause of disintegration any gradual progressive alteration in the atom during its period of existence, as, for example, was at one time suggested, a gradual radiation of internal energy by the electrons in their orbits within the atom. So far, we must admit, the cause of atomic disintegration remains unknown, although Lindemann (*Phil. Mag.*, 1915, [vi], **30**, 560) has attempted, with some success, to frame a theory to account for it.

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* The shortest wave-length so far resolved by the crystal reflection method is 0·072 Å. in the spectrum of the γ-rays of radium-*C*. Ishino and Rutherford have recently concluded, however, that the main γ-radiation of radium-*C* must have a wave-length lying between 0·02 and 0·007 Å. (*Phil. Mag.*, 1917, [vi], 33, 129; 34, 153.)

Branch Series.

The development of the various radioactive sequences revealed that sometimes the series branches, and that in the change of one radio-element sometimes two products result, in general, in different amounts. Thus the uranium series at one point branches into the radium and actinium series, in proportion 92 to 8 out of 100 atoms disintegrating. Again, in the case of radium-*C* and thorium-*C* a similar branching occurs, and here in one branch an α-ray change is followed by a β-ray change, and in the other branch the sequence is reversed. These cases are sufficiently explained if it be supposed that two simple radioactive changes are in progress in the same substance simultaneously, and that each obeys the law of simple change as though the other did not occur. The distribution of the original substance into the two products is then proportional to the relative rates of the two changes. If λ_1 and λ_2 are the radioactive constants of the two changes, the proportion between the two products is as λ_1 to λ_2, and the constant of the double change as a whole, $\lambda_1 + \lambda_2$. For thorium-*C*, the ratio is as 65 to 35, but for radium-*C* 99·97 to 0·03. The first is relatively easy, but the second extremely difficult to follow experimentally. It is, for example, impossible to follow further what occurs to the minor branch owing to the minuteness of the quantity of material, and although this has to be represented as not further changing, we have only negative evidence to go on. This branching is very important as showing how from one element two products or more in very different quantity may result, and may be the explanation of the excessive rarity of certain of the elements in nature.

History of the Analysis of Matter.

The second, and in many respects even more revolutionary phase in the development of the study of radioactive change arose out of the chemical characterisation of the successive products, but some historical comment on the various influences which have gone to shape the current conception of the chemical element may be of interest before dealing with this development.

The analysis of matter into different chemical elements was at first concerned with known materials obtainable in abundance. The question, then, was not as to the existence or otherwise of certain elements, but whether certain thoroughly well-known substances were elements or compounds. Boyle's original celebrated definition was a purely practical one. That was to be regarded as elementary which could not by any means be separated into different substances. Almost at once, however, there crept into the interpretation of this conception two fallacies, or two aspects of the same fallacy, implicit in all the later characterisations of the elements, right up to the present time, namely, first that chemical analysis was necessarily the most fundamental and searching kind of material analysis, known or to be discovered, and, secondly, that chemical compounds were necessarily more difficult to resolve than simple mixtures. *Any* means soon came to mean any chemical means, and the element, in consequence, the chemical element. So was taken the first step which ultimately was to make the term *chemical element*, as it is at present understood, denote a definite but highly complex chemical conception, incapable of being defined or even understood without long years of training in the science, and totally different in every single respect from what a plain man or a beginner in the subject might reasonably suppose the term element ought to connote. The elementary and even the homogeneous character has departed from the conception of the chemical element, but the conception remains, and, whatever we choose to call it, will remain. The criterion of the chemical element soon came to be, in fact, the possession of a unique chemical character, distinguishing it and sufficing for its separation from all other elements. To this Dalton added a new criterion, the magnitude of the weight of the atom of the element, and each element unique in chemical character (as it happened) proved also to possess a unique atomic weight.

The discovery of the periodic law introduced the idea of families of chemically analogous elements, the members of which recurred after regular intervals when the elements were arranged in order of atomic weight. With the exception of hydrogen, every element became one of a group all totally distinct, but with obvious similarities. Boyle's practical definition of the element as that which could not be further resolved, more and more, as the century advanced, fell into desuetude. It became replaced by a theoretical conception, to which subsequently I propose to apply the term "heterotope," meaning the occupant of a separate place in the periodic table of elements. With this place came to be associated the unique chemical character, unique atomic weight, and later unique spectrum. On the claims of a substance to the title of element, as in settling disputes as to what multiple of the equivalent was to be adopted as the atomic weight, the periodic law became the court of appeal. Did a claimant to the title of element fit into a vacant place in the family of related elements? If it did, not only was there no doubt as to its atomic weight, but it certainly could scarcely be an ordinary compound or mixture. Whatever the elements were, it was clear that they were all of a class, the limits of chemical analysis, and, if complex, then all probably of the same kind of complexity.

Incidentally, also, the periodic law showed that although there was a connexion between atomic weight and chemical character, there were exceptions, like tellurium and iodine, where the atomic weights appeared to have been reversed. This made it perfectly plain that it was merely a chance that no two elements happened to possess the same atomic weight. Dalton, as we shall come to describe, discovered in the atomic weight not merely a new atomic property, but a new class of atomic property which, until the present century, remained the only one of the kind known, and is concerned with a different region of the atom from that to which physical and chemical character, position in the periodic table, spectrum, and other identifying characteristics are to be referred.

The discovery of spectrum analysis led to the recognition of many new elements, cæsium and rubidium, thallium, indium, helium, and gallium all being so recognised before anything at all was known as to their other properties. In each case unique spectrum was later found to correspond with unique chemical character—except for the argon gases, all characterised by absence of chemical character—and unique atomic weight.

Again, the first fruits of the discovery of radioactivity were the recognition of the new elements polonium, radium, and actinium by their unique radioactive character in the first place. Then, in the case of radium, its claim to the title of element was confirmed, first by its exhibiting a unique spectrum, then by its possession of unique chemical character and atomic weight and by its occupying a vacant place in the periodic table. The emanations, next, as occupying a place in the family of argon gases, were easily characterised, and for the radium emanation unique spectrum was proved. Its origin from radium by loss of one α-particle gives the atomic weight as 222, which agrees with determinations of its density and rate of diffusion. The chemical characters of polonium and of actinium are different from those of the elements they most closely resemble. Polonium, or radium-*F*, by its close chemical analogy to both bismuth and tellurium, was characterised as an element of the sulphur family occupying the vacant place contiguous to bismuth. Actinium, by its resemblance in chemical character to the rare earths, and especially to lanthanum, although capable of being concentrated fractionally from that element, was reasonably supposed to occupy the vacant place in Group III, between radium and thorium. As will later appear evident, both these elements in due course may be expected to show unique spectra.

Further progress in the elucidation of the chemical character of successive products then underwent an abrupt and, at first, very puzzling change of direction. As member after member in the series was distinguished and characterised by its unique radioactive character, by its disintegration in definite and characteristic ways at definite and characteristic rates, no further *chemically* new elements were discovered. *Unique radioactive character does not always, as it did with radium, imply unique chemical and spectroscopic character.* The new members resembled known elements in chemical character so closely that they could not be separated from them by chemical analysis, although sharply differentiated from them by the radioactive properties. Radio-lead or radium-*D* cannot be separated from the lead which, being a product of uranium, accompanies it always in uranium minerals. Ionium, the direct parent of radium, cannot be separated from thorium; but the most instructive case, historically, which shows well how the new method of radioactive analysis serves to distinguish different elements, where chemical analysis fails, was the case of radiothorium.

Chemically Non-separable Elements.

Ramsay and Hahn, in the course of working up a large quantity of thorianite for radium, observed in fractionating the radium from the barium in the usual way that the activity of the material concentrated at both ends of the fractionation. The activity accumulating in the more soluble fractions was due to a new product, which they termed radiothorium. It produces thorium-X, the thorium emanation, etc., in successive changes. Naturally enough, they thought they had separated radiothorium by chemical processes from thorium, but they had not, for that, as we know, is quite impossible. Then Hahn found along with the other end fraction, containing the radium, a further new product, mesothorium, which is intermediate between thorium and radiothorium. The radiothorium they had separated from thorianite was not that present in the mineral when they started, but that which had re-formed from the mesothorium after it had been separated from the thorium in the mineral. Could any more elegant extension, not merely of knowledge, but of the means of obtaining knowledge, be imagined? Two different elements, thorium and radiothorium, which on account of their chemical resemblance could not be individually recognised, and in the original interpretation of the thorium disintegration series were taken as one, became individually knowable, because the latter is the product of the former through the intermediary of a third member, mesothorium, possessing chemical properties totally unlike either. Radioactive change thus became the means of a new analysis of matter, for which there is no counterpart outside the radio-elements.

In turn, mesothorium suffered analysis into two successive products, mesothorium-1 and -2, the first distinguished by long period of life and a rayless disintegration into the second, which has a short life and gives powerful β- and γ-radiation in its change into radiothorium.

I then found that mesothorium-1 was chemically non-separable from radium, a discovery also made by Marckwald at the same time, and in 1911 I pointed out that in an α-ray change, such as ionium into radium, radium into emanation, thorium into mesothorium-1, and other cases, the expulsion of the α-particle causes the radio-element to shift its place in the periodic table by two places in the direction of diminishing mass and diminishing valency, whereas in successive changes in which α-particles are not expelled, it frequently reverts to its former position, as, for example, radiothorium from mesothorium and lead from radio-lead.

To those actually engaged in the task of trying to separate the successive products of radioactive change by chemical analysis, it soon became clear that the chemical resemblances disclosed between certain of the members was such as to amount to chemical identity. The most obstinate cases of similarity previously known, among the rare earths, for example, cannot be compared with them. In all cases, radioactive methods afford the most delicate means for detecting the least alteration in the concentration of the constituents, and the most prolonged and careful attempts fail to produce a detectable separation.

At my request, Fleck undertook in my laboratory a systematic chemical examination of all the members of the series still imperfectly characterised, from the point of view of first finding which known element they most resembled and then finding whether or not they could be separated from that element. His researches were the means of finally unmasking the extreme simplicity and profound theoretical significance of the process of radioactive change. All the members of the series so far chemically uncharacterised he found to be chemically non-separable from one or other of the known elements, mesothorium-2 from actinium, radium-*A* from polonium, the three *B*-members and radium-*D* from lead, the three *C*-members and radium-*E* from bismuth, actinium-*D* and thorium-*D* from thallium.

Radioactive Change and the Periodic Law.

In February, 1913, K. Fajans in Germany, from electrochemical evidence, and in this country A. S. Russell and I independently, from Fleck's work, pointed out the complete generalisation which connects chemical character and radioactive change. In addition to the shift of two places in the periodic table caused by the expulsion of the α-particle, it was now clear that the expulsion of the β-particle caused a shift of one place in the opposite direction. Since the α-particle carries two atomic charges of positive electricity and the β-particle one atomic charge of negative electricity, the successive places in the periodic table must thus correspond with unit difference of charge in the atomic structure, a conclusion reached later for the whole periodic table, as far as aluminium, as the result of Moseley's investigations on the frequency of Barkla's characteristic *X*-radiations of the elements.

The non-separable elements, with identical chemical character, on this scheme were found all to occupy the same place in the periodic table, and on this account I named them isotopes. Conversely, the different elements recognised by chemical analysis should be termed "heterotopes," that is, substances occupying separate places in the periodic table, but themselves mixtures, actually proved or potential, of different isotopes, not necessarily homogeneous as regards atomic weight and radioactive character, but homogeneous as regards chemical and spectroscopic character, and also physical character, so far as that is not directly dependent on atomic mass.

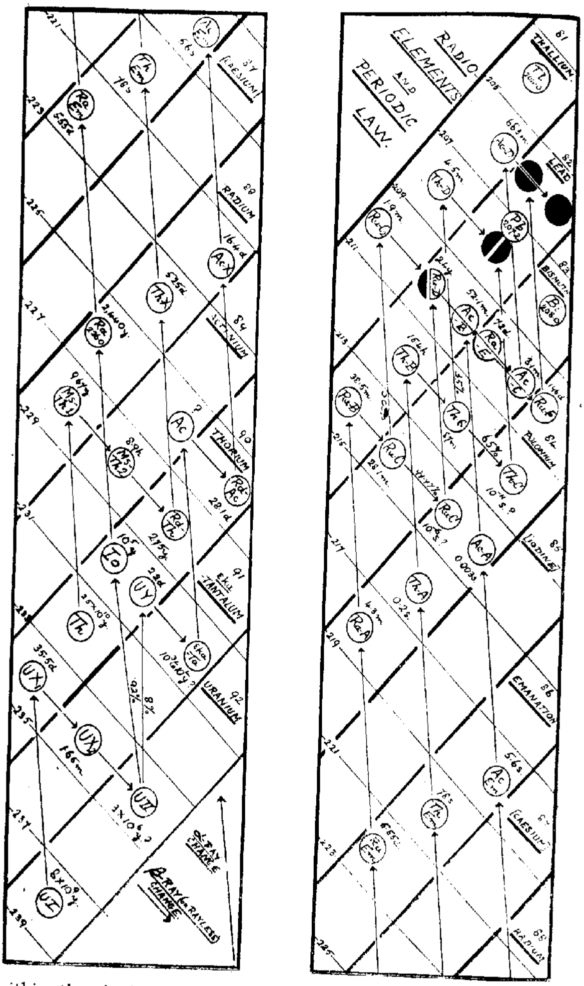
Spectra of Isotopes.

As regards the spectrum, the first indication that chemically non-separable elements probably possessed identical spectra arose out of the failure of Russell and Rossi and of Exner and Haschek in 1912 to detect any lines other than those of thorium in the spectrum of ionium–thorium preparations that might reasonably be supposed to contain an appreciable, if not considerable, percentage of ionium. The work of Hönigschmid on the atomic weight of ionium–thorium preparations has fully confirmed this view. The isotopes of lead of different atomic weight separated from uranium and thorium minerals have been found to possess identical spectra. For this element, lead, Rutherford and Andrade have shown that the secondary γ-radiation excited by the impact of β-rays on a block of ordinary lead gave by crystal reflection two lines identical in wave-length with the two strongest lines in the γ-ray spectrum of radium-*B*, an isotope of lead, as Fleck showed, of atomic weight 214. This is of importance as indicating that *X*-rays and γ-rays, although no doubt originating in a deeper region of the atom than the ordinary light spectrum, do not originate in the deepest region of all to which the weight of an atom and its radioactive properties are to be referred.

Description of the Figure.

The generalisation, brought up to date, is set forth in the accompanying figure, which is to be read at an angle of 45°, making the lines of atomic weight horizontal and the division between the successive places in the periodic table vertical. Starting from uranium and thorium, the series run in an alternating course across the table and extend over the last twelve places as far as the element thallium. At this point, it is interesting to note that the expulsion of an α- instead of a β-particle would have resulted in the production of an isotope of gold, and so literally have realised the goal of the alchemist. As it happens, a β-particle is expelled and lead results, so far as the changes have yet been traced, in all cases as the final product.

It has been necessary, in order to separate the series from one another, to displace the actinium series to the right and the radium series to the left of the centre of the places, but this displacement


RADIO-ELEMENTS AND PERIODIC LAW.
81 THALLIUM
82 LEAD
83 BISMUTH
84 POLONIUM
85 IODINE
86 EMANATION
87 CAESIUM
88 RADIUM
89 ACTINIUM
90 THORIUM
91 EKA-TANTALUM
92 URANIUM
α-RAY CHANGE
β-RAY or RAYLESS CHANGE
U I
U X₁
U X₂
U II
U Y
Io
Th
Ms Th₁
Ms Th₂
Rd Th
Ra
Ac
Rd Ac
Ac X
Th X
Ra Em
Th Em
Ac Em
Ra A
Th A
Ac A
Ra B
Th B
Ac B
Ra C
Th C
Ac C
Ra C'
Th C'
Ra D
Ra E
Ra F
Th D
Ac D
Pb
Bi
Tl

within the single place is not intended to express any physical significance; but for the fact that many members would be superimposed, they would all be represented in the centre of the places. The periods of average life, which are always 1·443 times the periods of half-change, are shown for each member above or below its symbol, a ? indicating that the period is estimated indirectly from the Geiger-Nuttall relation.

The figures at the head of each place represent the atomic numbers or number of the place in the periodic table, starting with hydrogen as unity, helium as 2, lithium as 3, and so on. Moseley found that the square-root of the frequency of the characteristic X-radiation of an element was, for the K-series of radiations, proportional to integers less by one than the atomic numbers. Strictly speaking, there is no means of determining the absolute value of the atomic number, but the starting point having been fixed for any one element, the others can then be found in terms of it. Moseley assumed the atomic number of aluminium as 13, as it is the thirteenth known element in the list starting with hydrogen as unity. It is unlikely that any new elements will be discovered between hydrogen and aluminium,* although if they were it would be necessary to alter the whole of the subsequent atomic numbers to correspond. For X-radiations of the other series, the square-roots of the frequencies are not proportional to integers even, although the differences are nearly integral for successive elements in the periodic table. The actual numbers in the figure, 92 for uranium, for example, are derived from the assumption that the atomic number of aluminium is 13, but it is well to remember that, although relatively to one another based on experimental evidence, the absolute value is to some extent arbitrary.

The Chemical Character of the Radio-elements.

The simple connexion between the sequence of radioactive changes and the chemical character of the products has effected an enormous simplification, not only in the theory, but also in the practice of radio-chemistry. The series extends over twelve places, two, namely, those in the families of the halogens and the alkali metals, being entirely skipped. In the ten occupied places are forty-three distinct types of matter, but only ten *chemical* elements. Seven of these ten, thallium, lead, bismuth, emanation, radium, thorium, and uranium, can now in every respect be considered, both chemically and spectroscopically, thoroughly well known. These seven places accommodate all but nine of the known radio-elements, and these nine, the isotopes of polonium, actinium, and ekatantalum, respectively, are the only members the chemistry and physics of which cannot be referred to well-known elements obtainable in sufficient quantity for ordinary chemical and spectroscopic examination.

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* The position of the stellar elements of Prof. Nicholson it is unnecessary to consider here, as the Chemical Society is shortly to be given a first-hand account of this fascinating question.

Of these three, polonium, although the element of which at present the chemistry is best known, is likely to remain the most difficult to bring into line with the others, for, although a vast amount of exact information has been obtained as to its reactions, it would seem to remain hopeless ever to obtain it in anything but infinitesimal amount owing to its relatively very short period.

The chemistry of actinium has been enormously simplified by the discovery that mesothorium-2 is isotopic with it, for the latter may be used as an indicator to show in what way the actinium distributes itself after any chemical treatment. Owing to its relatively small quantity as a branch product and to the fact that, itself, it gives no rays, the characteristic radioactivity of its products only making their appearance slowly after it has been separated, actinium has always been a difficult element to extract from the mineral and very easy to lose in chemical operations. There is now, however, another reason which will assist in the study of this element.

The Origin of Actinium. Ekatantalum.

The generalisation has now led to the elucidation of its origin and the discovery of its direct parent. From its constant association with uranium minerals, and the relative activity therein of its products in comparison with the activity of those of radium, it was considered to be a branch product of the uranium series, only 8 per cent. of the atoms of uranium disintegrating passing through the actinium series and 92 per cent. through the radium series. Its definite location in the periodic table, by virtue of its isotopy with mesothorium-2, made it clear that its parent must either be in the radium or the ekatantalum place, the former if it is produced in a β-ray change and the latter if it is produced in an α-ray change.

The ekatantalum place was vacant when the generalisation was first made, but it was necessary to suppose that uranium-X, like mesothorium, comprised two successive products, uranium-X_1 and uranium-X_2, both giving β-rays, and the latter occupying the vacant place in question. This prediction was confirmed within a few weeks of its being made by the discovery by Fajans and

Göhring of uranium-X_2, or brevium, a new member responsible for the more penetrating β-radiation given by uranium-X, and having a period of only 1·65 minutes. The possibility that actinium was produced in a β-ray change from an isotope of radium was experimentally disproved, and there remained only the second alternative, which was rendered the more probable by the existence of a member, uranium-Y, discovered by Antonoff, isotopic with uranium-X_1, and simultaneously produced with it from uranium in relative quantity such as is to be expected, if it were the first member of the actinium series. Uranium-Y, like uranium-X_1, gives soft β-rays, and hence its unknown product must be the isotope of uranium-X_2, and might also well prove to be the unknown direct parent of actinium in an α-ray change of long period.

During the year the missing element has been found in two independent investigations (Soddy and Cranston, *Proc. Roy. Soc.*, 1918, [*A*], **94**, 384; O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1918, **19**, 208). The problem as it presented itself to us was so to treat a uranium mineral as to separate an element, if present, which possessed the chemical character of the known but hopelessly short-lived uranium-X_2, using the latter as an indicator in trying possible methods beforehand. The method adopted, distillation at an incipient red heat in a current of carbon tetrachloride vapour and air, was found to be very effective in volatilising uranium-X_2 from uranium-X_1, and when applied to pitchblende it was found to give a product in which none of the known pre-emanation members of the disintegration series were present. Thus was obtained a preparation from which actinium was at first absent, but which, with the lapse of time, continuously generated actinium, as characterised beyond the possibility of doubt by means of its active deposit.

It should be mentioned that the exact point at which the uranium series branches has not yet been definitely ascertained, as there is a choice of alternatives, at present experimentally indistinguishable. Uranium-Y may be either the product of uranium-I or of uranium-II, and the latter alternative, which is that shown in the figure, is taken for the present as likely to be on the whole the more probable. The point can only be settled by the determination of the atomic weight of ekatantalum or actinium.

Independently, Hahn and Meitner obtained the parent of actinium from the insoluble siliceous residues left after the treatment of pitchblende with nitric acid by adding tantalum, and then separating it and purifying it by chemical treatment. They showed that it gave α-rays of range 3·314 cm. of air at *N.T.P.*, and, from this range, estimate its period to be from 10^3 to $2{\cdot}10^4$

years. There should therefore be sufficient of the element in uranium minerals to enable the spectrum, atomic weight, and chemical character of the pure substance to be determined in the same way as for radium. Its separation on a large scale will enable actinium itself to be grown in a pure state, analogously to the preparation of radiothorium from mesothorium, and so should allow the spectrum at least of actinium to be found.

With regard to the period of actinium, there is at present a real conflict of evidence, and so it is impossible to say whether our knowledge of actinium is ever likely to become as complete as that of radium, or to remain, like that of polonium, confined to what can be learned from infinitesimal quantities. Cranston and I, on certain assumptions, concluded from indirect evidence that the period of actinium was 5000 years, but Hahn and Meitner, on the other hand, state that they have obtained evidence confirming Mme. Curie's provisional estimate of the period as about thirty years, from the direct observation of the decay of the radiations of a sealed actinium preparation.

Atomic Weight of Isotopes.

It is clear that the periodic law connects, not primarily chemical character and atomic weight, but chemical character and atomic charge or atomic number, which alters its value by integers, not continuously, producing the step-by-step changes in chemical character which is at the basis of the analysis of matter into the chemical elements, or heterotopes. This atomic number is, however, the algebraic sum of positive and negative charges, so that the loss of the α-particle with its two positive charges and of two negative electrons as β-particles leaves its value unchanged and produces an isotope of the element having an atomic weight four units less than the original. Unique chemical character and unique spectrum reaction is no proof of homogeneity, and so we arrive at the conclusion that the chemical elements, so far considered homogeneous, may be mixtures of isotopes, possessing different atomic structure and stability, revealed when they undergo radioactive change and in some cases also different atomic weight. This, although within the scope of the Daltonian analysis of matter to detect, nevertheless, until radioactive investigations revealed this possibility, remained overlooked. In two cases, that of the isotopes of lead on the one hand, and of ionium and thorium on the other, this difference of atomic weight in elements spectroscopically and chemically identical has now been established by direct determinations.

The figure shows that, so far as these changes have been followed, they all terminate in the place occupied by lead, and, if this is the real, as distinguished from the apparent end in all cases, all the ultimate products are isotopes of lead with atomic weight between 210 and 206. The product of radium-C_2, in the branch claiming only 0·03 per cent. of the whole ultimate product of radium, with atomic weight 210, may be left out of account as being negligible, and also the product of the actinium branch for which the atomic weight is still uncertain; but the main products, namely, that of uranium with atomic weight 206, and both the thorium products in the two branches, with atomic weight 208, are different in different directions from that of common lead with atomic weight 207·2.

The conclusion that the ultimate product of thorium, as well as of uranium, was lead, was quite new and opposed to the opinion of those who had made a special study of the Pb/U and Pb/Th ratios of radioactive minerals of various geological periods. I found, however, that the atomic weight of the lead separated from Ceylon thorite was 207·7, and Hönigschmid confirmed this with a specimen of my material and obtained the figure 207·77. Just recently, from a specimen of lead separated from a Norwegian thorite by Fajans and his co-workers, he has found the value 207·90 (*Zeitsch. Elektrochem.*, 1918, **24**, 163). Whereas the same investigator, and also T. W. Richards and others, have found values for the atomic weight of lead separated from uranium minerals all lower than that of common lead, and in two cases from carefully selected minerals between 206·0 and 206·1. I found my thorite lead was denser than common lead in the same proportion as its atomic weight was greater, and the densities of the various specimens of uranium lead have been found by Richards to be less than that of common lead, the atomic volume for all varieties being constant. The spectra of these various isotopes have been repeatedly examined, but hitherto no differences whatever have been established.*

The atomic weight of a mixture of ionium and thorium was found by Hönigschmid to be 231·51 as compared with 232·12 for thorium, the spectra being identical and impurities absent in both specimens. The calculated value for the atomic weight of ionium is 230, and the evidence, so far as it yet goes, is in accord with the view that, in the mixture examined, about 30 per cent. was ionium and 70 per cent. thorium. By a simple comparison of the emanating power of the mixture with that of the pure thorium preparation under similar conditions, the proportion of ionium to thorium could be readily determined directly, since ionium does not give an emanation, and this unknown eliminated, but this has still to be done.

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* Haskins and Aronberg (*Proc. Nat. Acad. Sci.*, 1917, **3**, 710), for ordinary lead and uranio-lead of atomic weight 206·34, examining the strongest line, 4058, in the sixth order of spectrum obtained by a 10-inch grating, observed a constant difference of 0·0043 Å., but are themselves disposed to await further results before drawing any conclusions.

The Different Varieties of Isotopes and Heterotopes.

When isotopes, such as those just considered, possess different atomic weights, it is to be expected, although this has not yet been practically accomplished, that a separation by physical means, such as prolonged fractional diffusion, ought to be possible. Chlorine and other elements, the atomic weights of which depart largely from an integral value, seem to deserve a further physical analysis by this method. Sir J. J. Thomson's positive-ray method of gas analysis ought to be able to detect such isotopes of different atomic weight without separation, and at one time it seemed that neon had been so resolved, but this has not yet been confirmed.* It would be interesting also if the rotation of the salts of some optically active acid with different varieties of lead, separated from uranium and from thorium minerals, were examined. A difference is to be expected, although it is likely to be small, and possibly may be too minute to be detectable. Recent experiments at Harvard have shown that the refractive index of a crystal of lead nitrate is independent of the atomic weight of the contained lead, but the solubility, as is to be expected, is different, the molar solubility of different varieties being the same.

Isotopes need not, however, have different atomic weights. One of the clearest cases is in the two end-products of thorium, but, if the scheme is correct as regards the branching point of the actinium series, ionium and uranium-*Y*, actinium-*A* and radium-*C′*, actinium-*C* and radium-*E*, actinium-*B* and radium-*D*, and the actinium and uranium isotopes of lead, are other cases. These result by branchings of the series, and, since in the respective branches the amount of energy evolved in the successive changes is different, the internal energy of the various pairs must be different, although for them atomic weight as well as spectroscopic and chemical character are all identical. I recently suggested in the case of the two end-products of thorium that possibly only one of these survives in geological time, namely, that produced in the smaller quantity, and that the other continues to break up in changes as yet undetected (Royal Institution Lecture, May 18th, 1917; *Nature*, 1917, **99**, 414 and 433). This would account for the relative poverty of thorium minerals in lead, which was the original basis for the conclusion that lead was not the ultimate product of thorium. The point still remains experimentally untested. Isobaric isotopes of the character in question can only at present be distinguished if they are unstable and break up further, but they must be taken into account in any theoretical conception we form of the ultimate structure of matter. The accomplishment of artificial transmutation would reveal them if they existed, and the discovery of any new property, like radioactivity, concerned with the nucleus of the atom rather than its external shell, might also be the means of revealing differences of this character.

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* Mr. Ashton tells me this work is still being actively prosecuted at the Cavendish Laboratory.

On the other hand, the production of isobaric heterotopes is the ordinary consequence of β-ray changes, single or successive. Such heterotopes, possessing different chemical and spectroscopic character but the same atomic weight, have been recently termed *isobares* by A. W. Stewart (*Phil. Mag.*, 1918, [vi], **36**, 326), who, following Fleck's work on the chemical resemblance, not amounting to non-separability, between quadrivalent uranium and thorium, has drawn a parallel between them and elements existing in more than one state of valency, as, for example, ferrous and ferric iron.

The extent to which the study of radioactive change has enlarged the conception of the chemical element may be summarised by the statement that now we have to take into account in our analysis of matter, not only the heterobaric heterotopes before recognised, but also heterobaric and isobaric isotopes and isobaric heterotopes or isobares.

The Nuclear Atom.

I have attempted to present the most important facts of radioactive change without introducing any theory or hypothesis at all as to the structure of the atom. I think it important to keep the two matters distinct. Our knowledge of electricity, which in its modern phase may be considered to start from the relatively recent discovery of the electron, is still far too imperfect to enable any complete theory of atomic structure to be formulated. My task would be incomplete, however, if I did not refer briefly to the nuclear atom of Sir Ernest Rutherford, which may be regarded as the logical descendant of the earlier electronic atom of Sir J. J. Thomson. The weakness of the latter was that it took account essentially only of the negative electrons, and its attempt to ascribe the whole mass of the atom to these nearly massless particles involved the supposition that a single atom may contain hundreds of thousands of electrons. The actual number is now known to be rather less, as an average, than half the numerical value of the atomic weight. Although unsatisfactory in accounting for the mass of the atom on an electronic basis, it was much more in line with present views in accounting for chemical character and the arrangement of elements in the periodic table. The root idea that the successive elements in the table are distinguished by the increment of one electron in the outermost electronic ring, followed, as period succeeds period, by the completion of this ring and the formation of a new external one, so that members of the same chemical family have similar external ring systems, is still the most probable view yet advanced. In conjunction with the conception of the nucleus and the gradual unravelling of the various series of characteristic X-radiations, both experimentally and by mathematical analysis, it bids fair soon to give a definite concrete picture of the structure of all the different elements (compare L. Vegard, *Phil. Mag.*, 1918, [vi], **35**, 293).

As regards the deepest region of atomic structure, wherein radioactive phenomena originate, the nuclear atom is the only one proposed that has any direct experimental foundation. It is based on the deflections suffered by the α-particle in its passage through the atoms of matter, on the one hand, as Bragg showed many years ago, on the exceedingly slight deviation of the overwhelming majority of the α-particles, and, on the other, on the subsequently discovered large deviations suffered by a minute proportion. The nuclear atom is a miniature solar system, like most model atoms, the negative electrons occupying the atomic volume by their orbits around a relatively excessively minute central sun or nucleus, wherein the atomic mass is concentrated, and consisting of an integral number of atomic positive charges equal to the atomic number of the element, and the number of electrons in the outer shell. An α-particle is the nucleus of the helium atom, and, unless it passes very near the nucleus of the atom through which it penetrates, its path is practically undeflected. The few that chance to pass close to the exceedingly small but massive central nucleus are swung out of their path like a comet at perihelion, save that the forces at work are regarded as repulsive rather than attractive.

It appears from radioactive change that atomic disintegration occurs always in the central nucleus, both α- and β-particles originating therein. The atomic number of the element is its nett nuclear charge, the difference between the positive and negative charges entering into its constitution. Of all properties, mass and radioactivity alone depend on the nucleus; the physical and chemical character and the spectrum of an element originate in the outer shell. The character of the outer shell is fixed by the nett charge, not at all by the mass or internal constitution of the nucleus, and the integral variation of this charge from 1 to 92 gives the successive places of the periodic table. Expulsion of two β- and one α-particle in any order gives an isotope of the original element with atomic weight four units less. Isobaric isotopes resulting in branch changes differ only in the internal structure and stability of the nucleus. The atomic mass is the only nuclear property known before the discovery of radioactivity, and, except as regards this, the whole of physics and chemistry up to the close of the nineteenth century had not penetrated beyond the outer electronic shell of the atom. Even now, mass and radioactivity remain the sole nuclear properties known.

Conclusion.

Nemesis, swift and complete, has indeed overtaken the most conservative conception in the most conservative of sciences. The first phase robbed the chemical element of its time-honoured title to be considered the ultimate unchanging constituent of matter; but since its changes were spontaneous and beyond the power of science to imitate or influence to the slightest degree, the original conception of Boyle, the practical definition of the element as the limit to which the analysis of matter had been pushed, was left essentially almost unchanged.

The century that began with Dalton and ended with the discoveries of Becquerel and the Curies took the existing practical conception of the chemical element and theorised it almost out of recognition. The element was first atomised, and then the atom was made the central conception of the theory of the ultimate constitution of matter, on which modern chemistry has been reared, and from which its marvellous achievements, both practical and theoretical, have mainly sprung. The atom and the element became synonyms, related as the singular to the plural, and implicit throughout this century was the assumption that all the atoms of any one element are identical with one another in every respect. The only exception is in Sir William Crookes's conception of "meta-elements" as applied to the rare earths. Here the idea was rather that of a gradual and continuous difference among the different atoms of the same element, the properties of the latter being the mean of those of its individual atoms. Modern developments have tended definitely away from rather than towards this view.

The second phase in the development of radioactive change has now negatived each and every one of the conceptions of last century that associated the chemical element with the atom. The atoms of the same chemical element are only chemically alike. Unique chemical and spectroscopic character is the criterion, not of a single kind of atom, but rather of a single type of external atomic shell. Different chemical elements may have the same atomic mass, the same chemical element may have different atomic masses, and, most upsetting of all, the atoms of the same element may be of the same mass and yet be an unresolvable mixture of fundamentally distinct things. Present-day identity may conceal differences for the future of paramount importance when transmutation is practically realised. Then it may be found that the same element, homogeneous in every other respect, may change in definite proportion into two elements as different as lead and gold. The goal that inspires the search for the homogeneous constituents of matter is now known to be, like infinity, approachable rather than attainable. The word homogeneity can in future only be applied, qualified by reference to the experimental methods available for testing it.

All this, of course, does not in the least affect or minimise the practical importance of the conception of the chemical elements as understood before these discoveries. Every chemist knows the conception has had and will continue to have a real significance as representing the limit of the spectroscopic and chemical analysis of matter which remains, although it now is known to convey something very different from the original and natural conception of the chemical elements as the *l m n*'s of the material alphabet.

I.—*The Dilution Limits of Inflammability of Gaseous Mixtures. Part III. The Lower Limits of some Mixed Inflammable Gases with Air. Part IV. The Upper Limits of some Gases, Singly and Mixed, in Air.*

By Hubert Frank Coward, Charles William Carpenter, and William Payman.

Part III.

In Part I of this series of papers (Coward and Brinsley, T., 1914, **105**, 1859), the wide variation in the values assigned by different observers to the limits of inflammability of hydrogen and other gases in air was shown to be due to the very different criteria of inflammability used. The meaning of the term "inflammability" was therefore discussed, and it was concluded that inflammability could and should be regarded as a characteristic property of a gas mixture, apart from the precise means used for ignition and from the form of the vessel that might happen to be chosen for experiment. It was argued that a gaseous mixture should be termed inflammable *per se* at a stated temperature and pressure if, and only if, it were capable of indefinite self-propagation of flame, while the unburnt portion of the mixture was maintained at the stated temperature and pressure.*

In Part II (T., 1914, **105**, 1865), the lower limits of inflammability of hydrogen, methane, and carbon monoxide individually in air were examined experimentally by means of apparatus specially designed to enable the progress of flame to be observed in much wider and longer vessels than had been hitherto employed.†

The present paper records the results of experiments carried out to determine the lower limits in air of various mixtures of hydrogen, methane, and carbon monoxide taken two at a time or all three together, and, finally, of the complex mixture, a "town's gas."

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* This definition has been discussed by Burgess and Wheeler (T., 1914, **105**, 2591). Several other papers on the subject of "dilution limits of inflammability" have appeared since Coward and Brinsley's paper was published, but as they have not been concerned with the question of indefinite propagation of flame, but merely with the inflammation of very limited amounts of gaseous mixtures, they have no direct bearing on the present inquiry.

† Burrell and Oberfell (U.S.A. Bureau of Mines, *Technical Paper*, No. 119, 1915) have adopted a eudiometer of the same size as that used by Coward and Brinsley.

A simple formula, of purely additive character, has been put forward by Le Chatelier to connect the lower limits of single gases with the lower limits of mixtures of them. This formula, originally limited to binary mixtures, is generalised thus:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \ldots\ldots = 1.$$

where N_1, N_2, N_3 . . . are the lower limits, in percentages of the whole air mixture, for each combustible gas separately, n_1, n_2, n_3 . . . are the proportions, in percentages of the whole air mixture, of each combustible gas at the dilution limit. The percentage of total combustible gas present in the limit mixture is thus $L = n_1 + n_2 + n_3 + \ldots$

This formula enables the lower limit, L, of a combustible mixture to be calculated from the dilution limits of its several constituents. If the proportions of each of the combustible constituents are p_1, p_2, p_3 . . ., so that $p_1 + p_2 + p_3 + \ldots = 100$, a simple transformation gives its dilution limit in air as

$$L = n_1 + n_2 + n_3 + \ldots\ldots = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \ldots\ldots}$$

The physical meaning of the formula may be best appreciated by the consideration of a particular case. A mixture of air, carbon monoxide, and hydrogen which contains one-quarter of the amount of carbon monoxide necessary to form a lower limit mixture, together with three-quarters of the amount of hydrogen necessary, will be a lower limit mixture. In other words, the lower limits of inflammability form a series of inflammability equivalents for the individual gases of a mixture.

It may also be deduced from the formula that lower limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits.

Experimental support for the formula rests on observations by Le Chatelier (*Ann. des Mines*, 1891, [viii], **19**, 388) with three mixtures of methane and coal gas, by Le Chatelier and Boudouard (*Compt. rend.*, 1898, **126**, 1344) with three mixtures of hydrogen and carbon monoxide and with one mixture of acetylene and carbon monoxide, and by Eitner (Habilitationsschrift, München, 1902) with hydrogen and carbon monoxide in equal volumes and with coal gas. The difference between the calculated and the observed dilution limits rarely reached one twenty-fifth part of the combustible mixture. None of these experiments, however, was carried out in apparatus large enough to indicate whether the mixtures used were capable of continued propagation of flame. Thus, Le Chatelier and Boudouard used for the lower limit of hydrogen in air the figure 10 per cent., whereas the recent experiments have shown that mixtures containing upwards of 4·1 per cent. of hydrogen are capable of propagating flame apparently indefinitely in an upward direction. Le Chatelier had, in fact, found that the 10 per cent. hydrogen mixture was the weakest which would propagate flame downwards through a somewhat narrow tube. It is only necessary to ignite from below to produce a self-propagating flame in mixtures considerably weaker in hydrogen.

The experiments now to be described were therefore carried out in the eudiometer previously described (Coward and Brinsley, *loc. cit.*), 1·8 metres (6 feet) in length and 30 cm. (1 foot) square in section, with a capacity of 170 litres.

In each case, the mixtures under experiment were saturated with moisture at 18—19°, and were maintained at approximately atmospheric pressure during inflammation. The source of ignition was a spark gap of variable length between small platinum spheres. A 6-inch Apps coil with two, four, or six storage cells was used to produce single sparks. The various gases were prepared in a state of purity, and each mixture with air was made to the desired composition, which was checked by the analysis of samples taken just before firing.

EXPERIMENTAL.

The lower limits of a number of mixtures of hydrogen, carbon monoxide, and methane, taken two or three together, and also of a "town's gas," are recorded in table I (p. 30), together with the lower limits calculated by means of the Le Chatelier formula from the limits of the individual gases.

Several of the experimental results differ from those calculated by amounts exceeding the errors of observation and experiment; nevertheless, the formula gives a useful approximation over the whole range of mixtures examined, and may be applied, therefore, to water gas and to coal gas, as well as to town's gas.

The most striking anomaly was shown by the mixture containing 10 per cent. of hydrogen and 90 per cent. of carbon monoxide, where the large difference was in the opposite direction to that usually noted. This anomaly was more pronounced in experiments with the same mixture in a narrower tube (5 cm. diameter).

TABLE I.

Composition of gas (before admixture with air).			Lower limit of inflammability in air.		
Hydrogen.	Carbon monoxide.	Methane.	Observed. Per cent.	Calculated. Per cent.	Difference. Per cent.
100	—	—	4·1	—	—
75	25	—	4·7	4·9	−0·2
50	50	—	6·05	6·2	−0·15
25	75	—	8·2	8·3	−0·1
10	90	—	10·8	10·4	+0·4
	100	—	12·5	—	—
—	90	10	11·0	11·1	−0·1
—	75	25	9·5	9·6	−0·1
—	50	50	7·7	7·7	0·0
—	40	60	7·2	7·1	+0·1
—	25	75	6·4	6·5	−0·1
—	—	100	5·6*	—	—
25	—	75	4·7	5·0	−0·3
50	—	50	4·6	4·7	−0·1
75	—	25	4·1	4·4	−0·3
90	—	10	4·1	4·2	−0·1
100	—	—	4·1	—	—
33·3	33·3	33·3	5·7	6·0	−0·3
55	15	30	4·7	5·0	−0·3
"Town's gas" †			5·35	5·36‡	0·0

* This figure is chosen, rather than the lower value given by Coward and Brinsley (*loc. cit.*, p. 1885) for the reason stated on page 1877 of that paper: ". . . the flames of mixtures containing 5·3 to 5·6 per cent. of methane are very sensitive to extinction by shock . . . a 5·6 per cent. mixture will invariably propagate flame when the shocks are no greater than those occasioned by the somewhat violent bubbling of gas through water . . . (but) when the circumstances are such that a tranquil passage is assured, 5·3 per cent. is the lower limit of inflammability of methane in air." In none of the present experiments with methane mixtures did we observe the curious tranquil passage of flame noted with the 5·3 per cent. methane mixture, so that 5·6 per cent. seems the correct figure to employ for calculations in connexion with these experiments.

† Composition of the "town's gas": C_6H_6, etc., vapours=0·8. CO_2=2·6. O_2=0·5. C_2H_4 etc.=2·8. CO=14·1. H_2=46·6. CH_4=19·4. C_2H_6=4·0. N_2=9·2 per cent. The benzene, etc., vapours were estimated by the determination of their partial pressures, by Burrell and Robertson's method (*J. Ind. Eng. Chem.*, 1915, **7**, 669).

‡ For calculating this figure, the following lower limits of the individual gases were used: Hydrogen, carbon monoxide, and methane, as in table I, ethylene 3·4 per cent. (Eitner), ethane 3·1 per cent. (Burgess and Wheeler), benzene 1·4 per cent. (Kubierschky). The last three values represent results obtained in small vessels, but may probably be safely used in view of the comparatively small amounts of the three gases present in the "town's gas."

The non-inflammable constituents of the town's gas amounted to 12·3

A brief reference to the general character of the flames is necessary. Inflammable mixtures rich in hydrogen, including the town's gas, gave thin vortex rings of flame, increasing in diameter as they rose through the first 30 or 40 cm., and then breaking into luminous segments, which subdivided into balls of flame. The latter rose, increasing in number, to the top of the vessel. The flames in mixtures somewhat below the lower limit were extinguished at some stage of their journey. The flames of these mixtures showed, in fact, similar behaviour to those described by Coward and Brinsley for pure hydrogen, but the luminosity was much enhanced. Inflammable mixtures containing no hydrogen gave thick rings which, as they progressed, developed into flames of strongly convex front spreading from side to side of the box; similar mixtures just below the limit of inflammability gave rings of flame breaking into striæ, which were extinguished in the next 50 or 100 cm. of their journey. The appearance of all the flames of mixtures is apparently compounded additively of those of the individual components.

There was no difficulty in deciding upon the figure for the limit within about 0·1 per cent.

Conclusions (Part III.).

The lower limits of inflammability, in air, of mixtures of hydrogen, carbon monoxide, and methane, taken two at a time or all together, and also the lower limits of water gas, coal gas, and town's gas, may be calculated with approximate accuracy from the lower limits of the individual gases by means of Le Chatelier's formula.

PART IV.

The Upper Limits of some Gases, Singly and Mixed, in Air.

The upper limits of inflammability of hydrogen, methane, and carbon monoxide severally in air have been investigated by a number of observers; their results are quoted in T., 1914, **105**, 1859. The hydrogen figures show the greatest range of variation, namely, from about 55 to 80 per cent. of hydrogen. The methane figures mostly lie between 12 and 17 per cent. of methane, and

per cent., which on the lower limit mixture represents only 0·66 per cent. of the whole. In view of the known slight influence on the lower limit of methane of the substitution of small amounts of carbon dioxide or nitrogen for equal amounts of air, it is safe to assume for the purposes of the calculation that the non-inflammable constituents of coal gas (and likewise of water gas) can be treated as air.

the carbon monoxide figures are in the neighbourhood of 75 per cent. of carbon monoxide.

The Upper Limit of Hydrogen.—Some preliminary experiments were conducted with the object of discovering whether the flames in mixtures just below the upper limit resembled the flames in mixtures just above the lower limit. If so, the apparent discrepancies between the results of earlier workers might be explained on the same lines as the discrepancies noted in lower limit figures. It was soon evident, however, that comparatively weak or short electric sparks, which were quite strong enough to ignite lower limit mixtures, were unable to inflame upper limit mixtures. Stronger sparks in the latter mixtures started flames which travelled throughout the whole mixture. This promised a clue to the main cause of discrepancy of the results of others, and by the use of igniting sparks of such variable strength as might well have been employed in ordinary laboratory practice, a range of results was obtained nearly as wide as those of the previous uncorrelated list. The experiments were carried out in a half-litre globe with a spark of variable length in the centre. A 6-inch Apps induction coil was used with a constant break, and the current in the primary was varied by using a battery of 2 to 12 volts. We have to acknowledge our indebtedness to Mr. F. Brinsley for conducting this series of experiments, the results of which are recorded in table II.

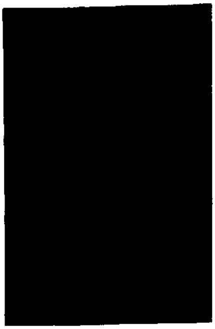
TABLE II.

Percentage of Hydrogen in Apparent Upper Limit Air Mixture.

	Voltage of accumulators.			
Spark gap.	2	4	8	12
1 mm.	57·5	—	67·0	—
2	—	—	70·2	—
4	—	—	71·2	—
8	70·2	70·7	71·2	72·2
16	—	—	72·5	—
20	—	—	—	74·5
32	—	—	73·5	—
45	—	—	—	75·5
56	—	—	73·5	—

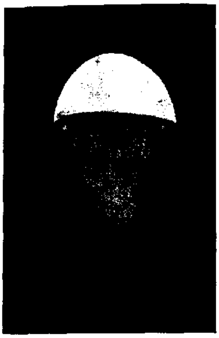
These figures suggest an upper limit of hydrogen–air mixtures in the neighbourhood of 75·5 per cent. of hydrogen, but the volume of gas used was much too small to indicate whether the flames observed were capable of indefinite self-propagation. Furthermore, the gases were confined, and so were not maintained under constant pressure during inflammation.

FIG. 1.



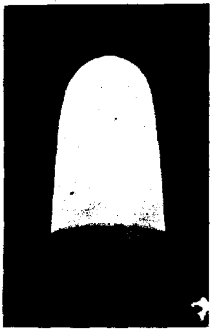
Hydrogen.

FIG. 2.



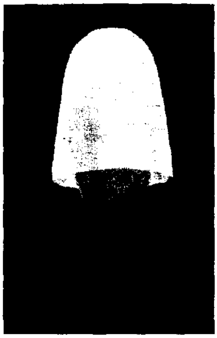
Methane.

FIG. 3.



Carbon monoxide.

FIG. 4



Methane and carbon monoxide mixture.

Upper limit flames, in tube of 5 cm. diameter.

[*To face page* 33.

A series of experiments was therefore carried out in a 15-litre bell-jar, just dipping under the surface of water, with a spark gap near the bottom of the mixture. With a suitable single spark, ignition was obtained with mixtures containing 73·1, 73·8, and 74·0 per cent. of hydrogen, but failed with 74·4 and 75·0 per cent. of hydrogen. The flames travelled rapidly throughout the whole mixture. The limit indicated was thus approximately 74·2 per cent. of hydrogen.

The next step in determining the true limit for continued propagation of flame was the use of long vessels. A tube 1·5 metres long and 5 cm. wide was used. Flame travelled rapidly through this tube with mixtures containing 71·2 and 71·4 per cent. of hydrogen. The appearance of this flame is indicated in Fig. 1. Mixtures containing 71·6 and 73·0 per cent. could not be ignited, or, if ignited, the flame was extinguished before it had travelled more than a few cm. from the spark.

In order to fix the upper limit precisely, it would be necessary to use vessels of dimensions comparable with those of the box previously described. This would involve the construction of a much stronger vessel than the one available, but at the time this was contemplated, the experiments had to be abandoned, and opportunities for continuing them will not be available in the near future.

It is, however, certain that the upper limit of hydrogen is somewhat higher than 71·5 per cent.; it is probably near to 74·2 per cent.

The Upper Limit of Methane.—In the 15-litre bell-jar, mixtures containing 15·1 and 15·3 per cent. of methane propagated flame, of a reddish-brown colour edged with blue, upwards throughout the mixture. A 15·5 per cent. mixture could not be ignited, but when a rapid succession of sparks was passed, a blue flame-cap was observed above them.

In the 1·5-metre tube, mixtures containing 14·4, 14·7, 15·0, and 15·1 per cent. of methane propagated flame throughout the tube; with a 15·2 per cent. mixture, a flame was initiated, but was extinguished after passing some cm. up the tube. In each case, the flame seemed to consist of two distinct portions, the uppermost blue with a convex front, followed by a reddish-brown conical tail, which suggested a secondary reaction of combustion (see Fig. 2). The limit for indefinite propagation is therefore more than 15·1 per cent., and probably approaches 15·4.

This conclusion is supported by the experiments of Burrell and Oberfell (*loc. cit.*), who used for upper limit experiments on methane an iron pipe 30 cm. (12 inches) in diameter, 2·1 metres

(7 feet) high, with a series of glass windows. Their experiments showed the upper limit to lie between 15·0 and 15·4 per cent. for upward propagation of flame.

The Upper Limit of Carbon Monoxide.—In the 15-litre bell-jar, flames travelling rapidly upwards through the whole of the mixture were obtained when 73·7 and 74·0 per cent. of carbon monoxide was present. Flames were initiated in 74·5 and 75·0 per cent. mixtures, but were extinguished after travelling a short distance. A 75·2 per cent. mixture gave only a blue halo round the spark.

In the 1·5-metre tube, a flame travelled up through a 72·9 per cent. mixture, but no more than a tongue of flame was obtained with a 73·1 per cent. mixture. The walls of the tube evidently exerted a notable cooling influence. The self-propagating flame had a strong convex front, was blue with a bright whitish-blue edging, but had no "tail," as was the case with methane flames (see Fig. 3).

The limit for indefinite propagation is therefore more than 73·0 per cent., and probably approaches 74·2 per cent.

Applicability of the Mixture Law to Upper Limits of Inflammability.

The additive character of the lower limits of inflammability was expressed by Le Chatelier in a formula quoted above (p. 28). The validity of a similar formula for the upper limits of mixed combustible gases in air has been obscured by experiments with hydrogen–air mixtures in which the sparks were insufficiently strong, and therefore the figures obtained represented, not the limiting composition for the propagation of flame, but the limiting composition for the initiation of flame by the sparks in use. It is shown below that the following formula holds approximately for the upper limits of mixtures of hydrogen, methane, and carbon monoxide, two or three at a time:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \;.\;.\;.\;.\;.\;. = 1$$

where n_1, n_2 . . . represent the proportions, in percentages of the whole air mixture, of each combustible gas, at the upper limit, N_1, N_2 . . . represent the upper limits, in percentages of the whole air mixture, of each combustible gas separately.

For reasons stated above, the experimental apparatus available did not combine the desirable width with the desirable length, and the choice lay between a bell-jar and a longer but narrower lass tube (1·5 metres long, 5 cm. in diameter). The latter was hosen because it enabled a flame to be observed travelling far nough from the original source of ignition; the disadvantage of arrowness was not great, for the limits observed in the tube were ower than those indicated by the wider bell-jar by a not very onsiderable amount. (For hydrogen, 2·7 on 74·2 per cent.; for ethane, 0·25 on 15·4 per cent.; for carbon monoxide, 1·2 on 4·2 per cent.)

The limits observed in the tube are recorded in table III.

TABLE III.

	Percentage composition of gas (before admixture with air)			Upper limit of inflammability, in air.		
	H_2.	CH_4.	CO.	Observed.	Calculated.	Difference.
ingle gases ...	100	—	—	71·5	—	—
	—	100	—	15·1	—	—
	—	—	100	73·0	—	—
inary mixtures.	48·5	51·5	—	22·6	24·4	−1·8
	50	—	50	71·8	72·5	−0·7
	—	50	50	22·8	25·0	−2·2
ernary mixture	33·3	33·3	33·3	29·9	31·9	−2·0
oal gas	See footnote.*			30·9	28·8†	+2·1

* Composition of the coal gas. C_6H_6, etc. = 1·2; CO_2 = 0·1; O_2 = 0·1; $_2H_4$ = 2·9; CO = 7·3; H_2 = 50·6; CH_4 = 29·7; C_2H_6 = 3·2; N_2 = 4·9 per cent.

† For the calculations, the upper limits of hydrogen, methane, and carbon nonoxide given in the table were used, together with the values C_6H_6 = 4·7 Roszkowski); C_2H_4 = 22·0; C_2H_6 = 10·7 (Burgess and Wheeler, ignition entrally in large globe. Private communication).

Analyses of the residual gases showed that mixtures just below the upper limit propagated flames which consumed the whole of the oxygen, and therefore passed through the whole of the mixture. This behaviour is in sharp contrast with that of lower limit mixtures, in which self-propagating flames may leave unconsumed a considerable fraction of the mixture.

Figs. 1, 2, and 3 show that the upper limit methane flames are characterised, in contradistinction from the hydrogen and carbon monoxide flames, by the possession of flame tails. Mixtures containing methane with carbon monoxide or hydrogen and air also exhibit the remarkable tail, which suggests a secondary reaction (see Fig. 4). Evidence as to the nature of this reaction should be readily obtained by an examination of the interconal gases, but the opportunity of attempting this experiment has not presented itself.

Conclusions (Part IV.).

The upper limits of inflammability in air, saturated with water at 18—19°, of hydrogen, methane, and carbon monoxide are in the neighbourhood of 74·2, 15·4, and 74·2 per cent. respectively.

The upper limits in air of mixtures of these gases, taken two or three at a time, and also the upper limit of coal gas, may be calculated with approximate accuracy by means of a simple formula of an additive character.

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II.—*The Propagation of Flame through Tubes of Small Diameter. Part II.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

IT is a common practice at collieries to test the safety of the miners' flame lamps, before they are taken underground, by introducing them into an inflammable mixture of coal-gas and air.

It is known that the speed of propagation of flame in mixtures of coal-gas and air can be considerably faster than in any mixture of methane and air. Since any inflammable mixture into which a miner's lamp may accidentally be introduced in the practice of coal mining is produced exclusively by fire-damp, and since it is a rare occurrence for fire-damp to contain even traces of any inflammable gas other than methane, the use of mixtures of coal-gas and air for testing the security of a lamp for use underground is justifiable only on the grounds of providing an adequate "margin of safety." The use of coal-gas becomes unjustifiable if the margin of safetv thereby provided is excessive; for every additional protective device embodied in the construction of a miner's flame safety-lamp militates against the proper ventilation of the lamp, and therefore diminishes its light-giving power.

It is thus of importance to be able to make an exact comparison between the speeds of propagation of flame in mixtures of coal-gas and air and fire-damp, or methane, and air under similar conditions of experiment. Furthermore, since the rapid speed of flame in coal-gas–air mixtures is, presumably, due mainly to the hydrogen contained therein, and since different qualities of coal-gas contain different proportions of hydrogen, it is necessary to obtain information regarding the effect of varying the proportions of the constituent gases in coal-gas on the speed of propagation of flame in its mixtures with air.

Following the same methods of experiment as with mixtures of fire-damp and air (T., 1918, **113**, 656), the speeds of the uniform movement of flame in mixtures with air of coal-gas, hydrogen, and a 1:1 methane–hydrogen mixture have been determined in glass tubes of different small diameters for comparison with the results obtained with fire-damp–air mixtures in similar tubes. Comparative experiments have also been made on the projection of flame through brass tubes of small diameter.

For the experiments with mixtures of coal-gas and air, a supply of gas from the main was stored over alkaline water in a metal gas-holder of 70 litres capacity; and the mixtures with air were made in smaller glass gas-holders from this supply. In this manner, variations in the composition of the coal-gas, such as would have occurred had the gas for each mixture been drawn direct from the main, were avoided.

Rather more gas was required to complete the series of experiments than was anticipated, so that it was found necessary to recharge the storage-holder before all the information desired was obtained.

From one point of view this was unfortunate, for the second charge of gas differed slightly in composition from the first, and mixtures with air of the one could not be directly compared with mixtures with air of the other. From another point of view, however, the enforced use of samples of coal-gas of different compositions was not to be regretted, for there were found to be marked differences in the speeds of propagation of flame in mixtures with air of the two qualities of gas. This observation led at once to the determination of the speeds of flame in mixtures with air of what may be termed a "synthetic coal-gas," containing equal parts by volume of methane and hydrogen. The results obtained, taken in conjunction with the known values for methane–air and hydrogen–air mixtures under the same conditions of experiment, are of considerable theoretical interest, whilst they should also prove of practical value.

According to Le Chatelier ("Le Carbone," p. 266. Paris, 1908), if several combustible gases are mixed together with air, the following relation exists at the lower limit of inflammability of the mixture, between the limits of inflammability N and N' of each of two gases and their proportions n and n' in the limit mixture:

$$n/N + n'/N' = 1.$$

Coward, Carpenter, and Payman have shown (this vol., p. 28) that this formula can be applied with considerable accuracy to a number of mixtures of gases, and that it holds also at the upper limit of inflammability.

The formula implies that if a limit mixture with air of one inflammable gas is mixed in any proportion with a limit mixture with air of another inflammable gas, a limit mixture results. Another way of stating the relation, in an expanded form, is as follows:

$$L = 100 / \left(\frac{a}{L_a} + \frac{b}{L_b} + \ldots\ldots \right) . \quad . \quad . \quad . \quad \text{(i)}$$

By means of this equation, the limiting percentage, L, for a mixture of gases can be found directly from the known limits of the individuals; a, b, . . . being the percentages of the individuals in the mixed inflammable gases, and L_a, L_b, . . . their respective limits.

The subject of the calculation of the limits of inflammability of mixed combustible gases is introduced here because a similar formula holds with remarkable accuracy (considering the nature of the phenomena under investigation) for calculating the speeds of flame in mixtures with air of a composite combustible gas like coal-gas, the speeds in mixtures of the individual gases with air being known. The formula is:

$$S = \frac{a + b + \ldots\ldots}{a/S_a + b/S_b + \ldots\ldots} \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

in which S is the speed required; a, b, . . . the percentages of the different combustible gases in the mixed gas (coal-gas, for example); and S_a, S_b, . . . the corresponding speeds of flames in mixtures of the individuals with air.

This formula necessarily finds its readiest application in the calculation of the speeds in distinctive mixtures, namely: (1) the limit mixtures, upper and lower, in which the speed of flame is slowest; and (2) the mixtures in which the speeds of flame are fastest. For such mixtures, the agreement between calculated and observed speeds is close.

In the table that follows are given: (1) the limits of inflammability, with horizontal propagation of flame in a glass tube 9 mm. in diameter, for hydrogen, methane, and a mixture of equal parts of hydrogen and methane; and (2) the speeds of the uniform movement of flame, in a horizontal glass tube 9 mm. in diameter, with the lower- and upper-limit mixtures and in the mixtures with the fastest speeds of flame, for hydrogen, methane, and the 1:1 hydrogen–methane mixture. The calculated limits and speeds for the hydrogen–methane mixture, as determined by equations (i) and (ii), respectively, are also given.

		Limits. Per cent.		Speeds of uniform movement of flame. Cm. per second.		
		Lower.	Upper.	Lower-limit mixture.	Mixture with fastest speed.	Upper-limit mixture.
Hydrogen		6·7	65·7	8·3	430	(50)
Methane		7·8	11·6	32·6	49	35·6
Hydrogen–methane mixture	(Obs.)	7·2	19·6	13·7	96	17·1
	(Calc.)	7·2	19·7	13·2	90	(42)

The value obtained for the speed of propagation of flame in the upper-limit mixture of hydrogen and air is not the true value, which should approximate to that of the speed in the lower-limit mixture. The probable reason for the discrepancy is explained later. Omitting this value, and the calculated value for the speed of flame in the upper-limit mixture of hydrogen–methane–air based on it, it will be seen that there is a close correspondence between the calculated and the observed values for the limits and speeds.

With coal-gas, the gases that preponderate are hydrogen and methane, which in the two samples, *A* and *B*, used for these experiments totalled 83·5 and 85 per cent. respectively. Ignoring the other gases, calculation according to equation (ii) gives 106 and 96 cm. per second, respectively, as the maximum speed obtainable during the uniform movement of flame in a tube 9 mm. in diameter in mixtures of each sample of coal-gas with air. The speeds as determined by chronographic means were 106·2 and 94 cm. per second.

The proportion of mixed gases to be added to air to give mixtures with the fastest speed of the uniform movement of flame can also be calculated, knowing the corresponding values for each individual gas. The fastest speed with mixtures of methane and air is obtained over the range 9·5—10·0 per cent. of methane; with mixtures of hydrogen and air, the range is 38—45 per cent. of hydrogen. Using the same type of formula as for calculating the limit mixtures, the "fastest speed mixtures" of air with mixed combustible gases are found to be as follows:

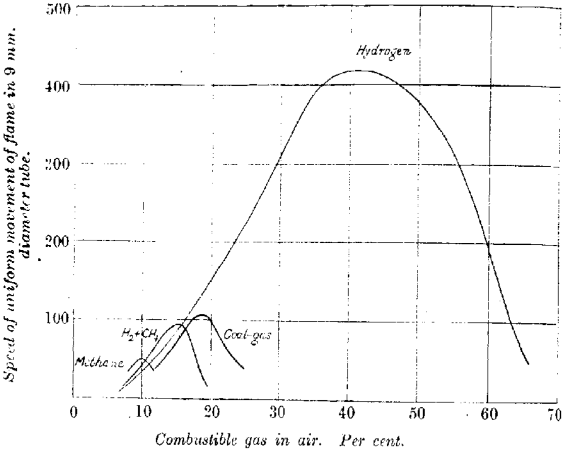
	Mixtures with air in which the speed of the uniform movement of flame is fastest. Per cent. of combustible gas.	
Combustible gases.	Calculated.	Observed.
Hydrogen–methane, (1 : 1)	15·2—16·3	15·0—16·0
Coal-gas A	17·5—18·8	18·0—19·0
Coal-gas B	16·3—17·5	16·5—17·5

If equation (ii) is expressed in the form

$$a/S_a + b/S_b + \ldots = \frac{a+b+\ldots}{S_{a+b+\ldots}}.$$

it is at once apparent that the inverse of the speed of flame in mixtures of a composite gas with air is a simple additive property of the inverse of the speed of flame in each constituent gas with air. In other words, the time taken for flame to spread through a given volume of a mixture of combustible gases with air, under the conditions of combustion during the uniform movement, is the mean of the times taken for flame to spread through the same volume of mixtures of each constituent gas with air if present alone.

Fig. 1.



No doubt this relation, which has been shown to hold true for the fastest and the slowest speeds of the uniform movement of flame, is true also, as suggested by the generalisation just stated, for intermediate speeds. So that, given the necessary data respecting the individual combustible gases, the behaviour of flame in any mixture of several with air can be deduced. The exposition of the validity or otherwise of this assumption, when three or more combustible gases in varying proportions are used, will form the subject of a subsequent communication.

In Fig. 1 are shown, plotted to the same scale, the speed–percentage curves, for the uniform movement of flame in a horizontal glass tube 9 mm. in diameter, for hydrogen and methane, for a 1:1 mixture of hydrogen and methane, and for coal-gas (sample *A*).

The curve for hydrogen is constructed from Haward and Otagawa's determinations (T., 1916, **109**, 85), with additional figures obtained near and at the limiting percentages. In this connexion, it should be noted that Haward and Otagawa, though they made no attempt to determine accurately the limits of inflammability for horizontal propagation of flame, considered that in a tube 9 mm. in diameter flame would not travel horizontally in mixtures containing less than 11·8 or more than 63·5 per cent. of hydrogen. Actually, the limits under the conditions thus specified are 6·7 (lower) and 65·7 (upper) per cent. It was found that when igniting mixtures near the limits of inflammability, great care had to be exercised to avoid disturbance at the mouth of the tube, and for that reason a lighted taper, such as was employed by Haward and Otagawa, which answered admirably over the range of mixtures studied by them, was unsuitable.*

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* The details of the determinations made to locate the limits of inflammability of hydrogen–air mixtures in a horizontal tube 9 mm. in diameter are as follow: the tube was 1·5 metres long and the mixtures were ignited by a secondary discharge across a 5 mm. gap 4 cm. from the open end of the tube.

Lower limit. Hydrogen, per cent.	Result.
9·4	Flame travelled throughout.
7·5	,, ,, ,,
7·1	,, ,, ,,
6·8	,, ,, ,,
6·6	Incomplete propagation of flame.

These results place the lower limit at 6·7 per cent. hydrogen. A mixture of this composition when tested failed three times to propagate flame, but on five occasions flame travelled throughout the length of the tube. The flames travelled very slowly and were only visible when the room was in complete darkness.

Upper limit. Hydrogen, per cent.	Result.
63·5	Rapidly moving flame throughout.
64·5	,, ,, ,,
65·0	,, ,, ,,
65·3	,, ,, ,,
	,, ,, ,,

With mixtures containing 66 per cent. or more of hydrogen a sharp report occurred on sparking, due to the rapid combustion of a mixture made poorer in hydrogen by diffusion between the point of ignition and the open end of the tube. Flame also travelled rapidly over short distances towards the closed end of the tube; thus, with 67·5 per cent. hydrogen the flame travelled 25 cm., and with 67·8 per cent. 10 cm. With 68 per cent. no flame could be

Attention should be directed to the slow speed, 8·3 cm. per second, at which flame could travel in a mixture of hydrogen and air at the lower limit, a fact which illustrates the well-known persistence of hydrogen flames. In conformity with the results obtained for other gases, it was expected that the flame in the higher-limit mixture would be equally slow. The fact that so high a speed as 50 cm. per second was recorded was due to the difficulty experienced in igniting the mixture before diffusion at the mouth of the tube could decrease the percentage of hydrogen there.

The coal-gas was made at the carbonising plant of the Experimental Station, and was not diluted with water-gas. The analyses of the two samples were:

	Sample *A*. Per cent.	Sample *B*. Per cent.
Benzene and higher olefines	1·2	1·6
Carbon dioxide	0·1	nil
Ethylene	2·9	2·8
Carbon monoxide	7·3	7·1
Hydrogen	50·6	47·0
Methane and higher paraffins	32·9	38·0
Nitrogen (by difference)	5·0	3·5

It will be seen that the difference between the two samples of gas lay almost entirely in the proportions of hydrogen and paraffins that they contained; and from a comparison between the speed–percentage curves for coal-gas *A* and the hydrogen–methane mixture given in Fig. 1, it is evident that the slower speed of flame obtained with coal-gas *B* as compared with coal-gas *A* is due to the higher methane-content of the former. For the highest speed obtainable with the hydrogen–methane mixture, which contained 50 per cent. of each constituent, is considerably slower than the highest speed obtainable with coal-gas *A*, which also contained 50 per cent. of hydrogen, but only 33 per cent. of methane.

The results obtained on the propagation of flame in horizontal glass tubes of smaller internal diameter than 9 mm. are recorded in the tables that follow. The determinations were made in the same manner, and the numbers in the table have the same significance, as in the experiments with methane and air (*loc. cit.*, p. 658), with which they should be compared.

observed to travel away from the open end of the tube. These results place the upper limit for self-propagation of flame between 65·3 and 66·0 per cent. hydrogen. The determination was completed as follows:

Hydrogen, per cent.	Result.
65·9	Flame travelled rapidly about 40 cm.
65·7	" " "
65·6	Complete propagation of flame.

TABLE I.

Coal-gas, Sample A.

Internal diameter of tube,	Coal-gas in mixture. Per cent.								
mm.	12·4	13·1	16·4	17·5	18·4	19·2	20·0	22·7	24·5
2·0	nil	nil	nil	nil	nil	nil	nil	nil	nil
3·0	(25)	(50)	—	—	81·3	—	—	nil*	—
4·2	(25)	49·6	—	—	87·3	—	—	nil*	—
5·0	(30)	53·5	—	—	98·1	—	—	35·3	—
6·0	(44)	55·5	—	—	99·1	—	—	40·6	nil*
7·1	(52)	58·7	86·8	97·7	103·7	102·7	90·3	50·6	nil*
8·0	(60)	59·2	87·4	98·8	104·2	103·9	91·8	57·0	29·8

TABLE II.

Coal-gas, Sample B.

Internal diameter of tube,	Coal-gas in mixture. Per cent.				
mm.	13·1	14·0	14·8	16·5	16·8
2·0	nil	nil	nil	nil	nil
3·0	nil	—	60	—	—
4·2	(35)	—	—	—	—
5·0	(35)	—	—	—	—
6·0	(41)	—	—	—	—
7·1	(52)	62·2	71·4	84·1	80·1
8·0	(57)	63·2	77·4	85·8	82·3

TABLE III.

Hydrogen–Methane, 1:1.

Internal diameter of tube,	Hydrogen–methane in mixture. Per cent.										
mm.	8·45	9·45	11·90	13·90	14·35	14·95	15·95	17·20	18·10	18·65	19·55
2·0	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
3·0	—	—	56·3	74·9	—	74·5	73·0	nil*	—	—	—
4·2	—	nil	57·9	75·9	—	—	—	46·1	nil*	—	—
5·0	—	(28)	59·4	83·1	—	86·0	84·0	53·5	nil*	—	—
7·1	(30)	38·7	63·0	85·1	88·0	95·8	94·1	74·1	43·3	nil*	—
8·0	(40)	39·4	69·5	87·1	90·7	—	—	75·8	49·4	34·2	nil*

* Flame travelled towards the open ends of the tubes, a distance of 3 cm.

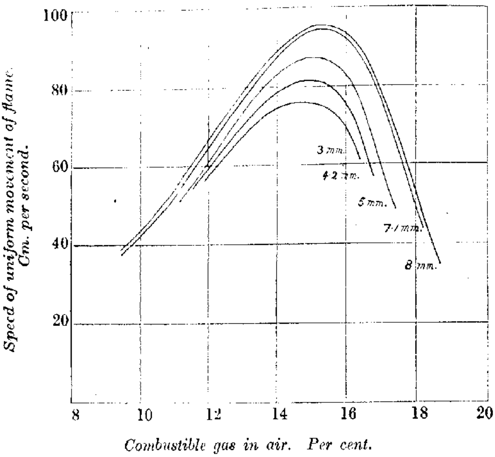
The results recorded in table III are shown as smoothed curves in Fig. 2, which illustrates the extent to which the "limits" are dependent on the environment of the inflammable mixture. It will be seen that the range of mixtures over which continued (horizontal) propagation of flame was possible became gradually restricted as the diameter of the tube was decreased, until with a

3 mm. tube it was less than half of that obtaining in a 9 mm. tube.

With a tube 2 mm. in diameter, no flame could travel away from the point of ignition, whatever the percentage of combustible gas present, an observation that applies also to the mixtures of coal-gas and air. With all mixtures of methane and air, a diameter of 3·6 mm. prevented the propagation of flame; whereas with hydrogen and air (30 per cent. hydrogen), Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 320) have recorded the propagation of flame in a glass tube only 0·9 mm. in diameter.

Complementary to these results are the results of experiments made on the passage of flame in mixtures of coal-gas and air through brass tubes, either open at both ends or arranged as extensions to a larger vessel, at the closed end of which the mixture was ignited. It is unnecessary to give the details of these experiments, which were conducted in the same manner and exhibited the same general features as the experiments with methane. It is sufficient to record that the flame in an 18 per cent. mixture of coal-gas *B* and air passed through 15—18 cm. length of brass tube of 4·4 mm. internal diameter placed horizontally and open at both ends, and was projected from a closed vessel (20 cm. long) through 13—15 cm. length of the same brass tubing. The corre-

FIG. 2.



sponding distances when a 10 per cent. mixture of methane and air was used were 7·5 and 3—4 cm. respectively.

The general conclusion to be drawn from these experiments as regards the testing of miners' safety-lamps is that "coal-gas" is an unsuitable gas to employ for that purpose, for the following reasons:

(1) Comparatively small variations in the composition of coal-gas affect the speed at which flame can travel in its mixtures with air. In particular, a reduction in the proportion of paraffins which it contains, such as is usually accompanied by an increase in the proportion of hydrogen when, as generally, carburetted water-gas is employed to dilute the coal-gas, enables a much higher speed of flame to be attained than can be given by mixtures of methane and air.

(2) Even with gas produced solely by the carbonisation of coal at normal retort temperatures, the speed of propagation of flame attainable is more than double that possible in mixtures of methane and air.

(3) It would seem that the ability of flame to pass through tubes or holes of small diameter is not dependent alone on its speed, although this is the main factor, but is to a certain extent a quality of the inflammable gas concerned. Flame in mixtures of hydrogen and air possesses the property of being able to pass through holes of very small diameter, and the presence of hydrogen in coal-gas confers this property in a certain degree on the flame in mixtures of the latter with air.

ESKMEALS,
CUMBERLAND.

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III.—*Mixtures of Nitrogen Peroxide and Nitric Acid.*

By WILLIAM ROBERT BOUSFIELD, K.C.

NITRIC acid and nitrogen peroxide are mutually soluble in certain proportions, and in other proportions give rise to a double layer. When to the simple binary mixture water is added, a more complex mixture arises. A systematic study of these mixtures was projected, beginning with the simple binary mixture and passing on to consider the modifications which are introduced by the addition of water. The present communication deals with the first part only of this research. The nitric acid and nitrogen peroxide for the research have been specially prepared by Nobel's Explosives Co., Ltd., with whose chief research chemist, Mr. Rintoul, I have been in consultation from time to time.

Nitrogen Peroxide.—Nitrogen peroxide absorbs moisture readily, and in the absence of excess of nitric acid appears to decompose according to the equation

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$

The presence of a very small quantity of water will therefore change the colour of liquid nitrogen peroxide to a dirty green, but traces of moisture may involve the presence of nitrogen trioxide without noticeable change of colour. Two samples of liquid nitrogen peroxide were supplied by Messrs. Nobel. Nearly all the work was done with sample No. 1, which was subsequently found to have contained traces of nitrogen trioxide. Sample No. 2 had been purified by distilling it with phosphoric oxide. The probable reactions which result in this purification appear to be

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5,$$
$$N_2O_5 + N_2O_3 = 2N_2O_4.$$

This sample, No. 2, may be regarded as pure liquid nitrogen peroxide.

In the meantime, before receiving this pure sample, I had used up sample No. 1 in nitric acid solutions and recovered it by distillation and rectification with a pear still-head. This sample, to which I may refer as No. 3, appears by the density given below to be nearly as pure as No. 2. This is probably due to the oxidation of the nitrogen trioxide by nitric acid, according to the equation

$$2HNO_3 + N_2O_3 = 2N_2O_4 + H_2O.$$

Thus with excess of nitric acid and very little water the reaction

$$N_2O_4 + H_2O = HNO_2 + HNO_3$$

appears to be reversed, and in the presence of excess of nitric acid the water appears to have no decomposing effect on the nitrogen peroxide.

As further evidence of this, the addition of a few drops of water to the orange-coloured liquid nitrogen peroxide turns it a dirty dark green, presumably due to the mixture of the blue nitrogen trioxide or nitrous acid with the orange nitrogen peroxide, but the addition of a few drops of nitric acid destroys the green and restores the orange colour.

The green colour cannot be eliminated by simple rectification, as the nitrogen trioxide and peroxide appear to pass off together, the resulting gas being of a somewhat deeper red colour than that of pure nitrogen peroxide. Nor does the addition of syrupy phosphoric acid help matters. Solid phosphoric oxide appears to be necessary to get rid of the nitrogen trioxide unless excess of nitric acid is added.

Another sample (No. 4), of a bulk of about half a litre, which had been accidentally contaminated with sufficient water to turn it to the dark green colour, was mixed with sufficient nitric acid to restore the orange colour and then distilled with phosphoric oxide. The resulting sample, No. 5, was of the same colour and density as the pure sample, No. 2. In the rectification of sample No. 4, the first few c.c. passed over green at a temperature at the top of the still-head of 19—20°. The bulk, which constitutes sample No. 5, distilled at 21·9±0·1°, which may be taken as the boiling point of pure liquid nitrogen peroxide.

TABLE I.

Specific Volumes of Samples of Nitrogen Peroxide.

	4°.	11°.	18°.
No. 1	0·67390	0·68110	0·68864
No. 2	0·67435	0·68172	0·68938
No. 3	0·67432	0·68168	0·68935
No. 4	—	—	0·68946
No. 5	—	0·68170	—

A set of density observations on sample No. 1 was taken at the temperatures given in table II, which gives the observed specific volumes and those calculated from the formula

$$v = 0{\cdot}66994 + 0{\cdot}0009767t + 0{\cdot}00000344t^2.$$

TABLE II.

Specific Volumes of Sample No. 1 at Various Temperatures.

t.	D.	v observed.	v calculated.	Difference.
0·08°	1·49250	0·67002	0·67002	±
7	1·47704	0·66703	0·67695	−8
11	1·46822	0·68110	0·68110	±
15	1·45909	0·68536	0·68536	±
18	1·45214	0·68864	0·68863	1
20	1·44750	0·69085	0·69085	±

For the pure sample No. 2 the specific volume–temperature curve derived from the three duplicated observations at 4°, 11°, and 18° is

$$v = 0{\cdot}67027 + 0{\cdot}0010075t + 0{\cdot}000003t^2,$$

which may be taken as giving the correct specific volume of pure nitrogen peroxide at temperatures from 0° to 20° within ±2 in the fifth place of decimals

Nitric Acid.—The nitric acid used was specially purified and sent to me by Messrs. Nobel with the following analysis:

Nitric acid	99·68	per cent.
Hydrochloric acid	0·007	,, ,,
Sulphuric acid	0·068	,, ,,
Nitrous acid........................	0·012	,, ,,
Mineral matter	nil	
	99·767	,, ,,

I have taken the percentage of water by difference as 0·233 per cent.

The densities of this acid at the temperatures indicated are:

4°.	11°.	18°.
1·5381	1·5254	1·5126

In calculating the strength of the various mixtures of nitric acid and nitrogen peroxide, to which reference is made later, the nitrous acid given in the above analysis has been reckoned as nitrogen peroxide, since, for the reasons above given, it is assumed that with very concentrated nitric acid the nitrous acid present is oxidised to give nitrogen peroxide and water.

In table III are given the resulting values of the specific volumes, derived from the density determinations.* P is the percentage by weight of nitrogen peroxide in the mixture. The temperature coefficients, α, from 4° to 11° and from 11° to 18°

TABLE III.

Specific Volumes of Mixtures of Nitric Acid and Nitrogen Peroxide.

				Temperature-coefficients.	
P.	v_4.	v_{11}.	v_{18}.	4—11° $\alpha \times 10^5$.	11—18° $\alpha \times 10^5$.
0	0·65015	0·65557	0·66113	77	79
1·2168	0·64839	0·65374	0·65920	76	78
8·021	0·63719	0·64211	0·64715	70	72
16·88	0·62372	0·62821	0·63291	64	67
26·09	0·61214	0·61655	0·62113	63	65
34·925	0·60445	0·60885	0·61346	63	66
37·60	0·60296	0·60743	0·61204	64	66
42·01	0·60112	0·60568	0·61044	65	68
43·71	0·60082	0·60543	0·61026	66	69
46·70	0·60088	0·60561	0·61059	68	71
48·66	0·60113	0·60599	0·61110	69	73
49·96	0·60145	0·60639	0·61161	71	75
51·37	0·60205	0·60715	0·61248	73	76
53·10	0·60341	0·60873	0·61436	76	80
93·86	—	—	0·68610	—	—
96·93	0·67305	0·68030	0·68786	104	108
98·49	0·67371	0·68098	0·68855	104	108
100·00	0·67435	0·68172	0·68938	105	109

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* The actual density determinations have been omitted at the request of the Publication Committee to save space.

TABLE IV.

Contraction of Mixtures of Nitric Acid and Nitrogen Peroxide.

	Contraction per c.c. of solution.			Contraction per gram of solution.		
P.	4°.	11°.	18°.	4°.	11°.	18°.
1·22	0·0032	0·0033	0·0034	0·0021	0·0022	0·0023
8·02	0·0234	0·0242	0·0251	0·0149	0·0156	0·0163
16·88	0·0489	0·0506	0·0521	0·0305	0·0318	0·0330
26·09	0·0724	0·0743	0·0763	0·0443	0·0458	0·0474
34·92	0·0896	0·0917	0·0938	0·0542	0·0559	0·0575
37·60	0·0934	0·0954	0·0976	0·0563	0·0580	0·0597
42·01	0·0985	0·1005	0·1025	0·0592	0·0609	0·0626
43·71	0·0997	0·1017	0·1036	0·0599	0·0616	0·0632
46·70	0·1008	0·1027	0·1044	0·0606	0·0622	0·0637
48·66	0·1011	0·1028	0·1044	0·0608	0·0623	0·0638
49·96	0·1011	0·1026	0·1040	0·0608	0·0622	0·0636
51·37	0·1005	0·1019	0·1031	0·0605	0·0619	0·0632
53·10	0·0988	0·0998	0·1005	0·0596	0·0607	0·0618
93·86	—	—	0·0023	—	—	—
96·93	0·0008	0·0009	0·0009	—	—	—
98·49	0·0004	0·0005	0·0006	—	—	—

are also set out in table III, as they give an important clue to the nature of the combination which is taking place in the mixture.

Another important matter bearing on this is the contraction which takes place at various constitutions of the mixture. The enthetic point, that is, the point of closest packing (see Bousfield, T., 1915, **107**, 1412), may be obtained by calculating the ratio of the volume of the constituents before mixture to the volume at the same temperature after mixture, which is

$$R = \frac{Pv_0 + (100 - P)w}{100v},$$

where v_0 = specific volume of nitrogen peroxide, w = specific volume of nitric acid, v = specific volume of the mixture.

It should be noted that $R - 1$ is the contraction per c.c. of solution formed, the values of which are set out in table IV.

In the same table are set out the values of the difference between the volume of a gram of the constituents before mixing and the volume after mixing, which is

$$\Delta = \frac{Pv_0 + (100 - P)w}{100} - v.$$

Consideration of the Results.—The results given in the tables are exhibited in Figs. 1, 2, 3, and 4, where they are set out on the values of P, the percentage by weight of nitrogen peroxide, as abscissæ. There are shown in :

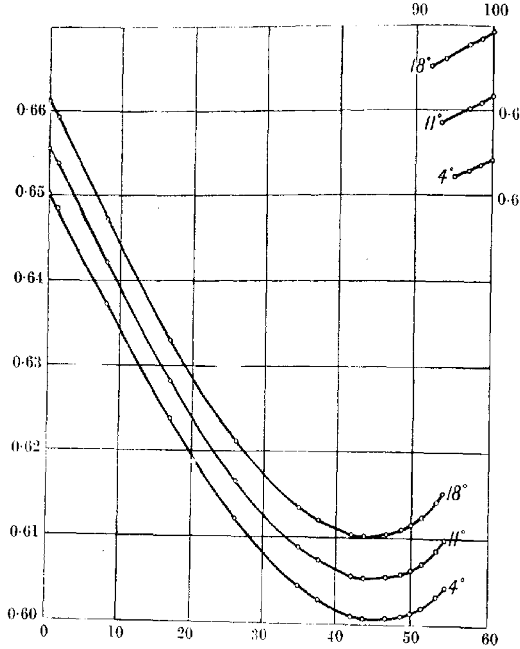
Fig. 1, the specific volumes of the mixtures.

Fig. 2, the values of $R-1$ near the maximum.

Fig. 3, the values of Δ near the maximum.

Fig. 4, the temperature coefficients for the intervals 4—11° and 11—18°.

FIG. 1.



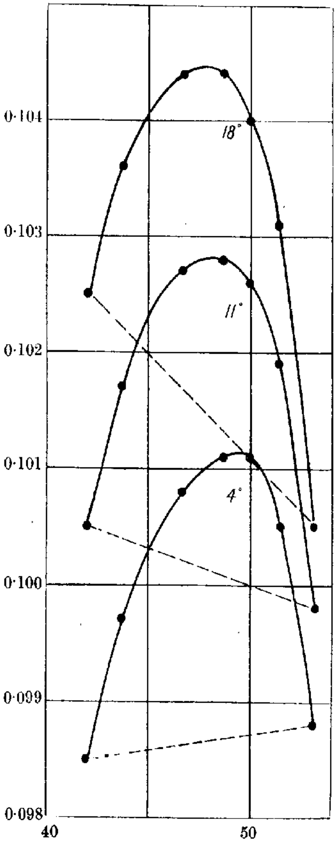
Specific volume of mixtures of nitric acid and nitrogen peroxide at 4°, 11° and 18°.

x = *Percentage of nitrogen peroxide.*
y = *Specific volume.*

The notable heat of evolution on mixing approximately equal weights of nitric acid and nitrogen peroxide (which it is proposed to determine accurately at a later stage) indicates a powerful combination. The minimum values of the specific volume curves give the same indication, showing a notable contraction of about 10 per cent. The minima do not, however, locate the exact composition. They occur:

for 4° at about 44·6 per cent.
for 11° ,, 44·2 ,,
for 18° ,, 43·8 ,,

Fig. 2.



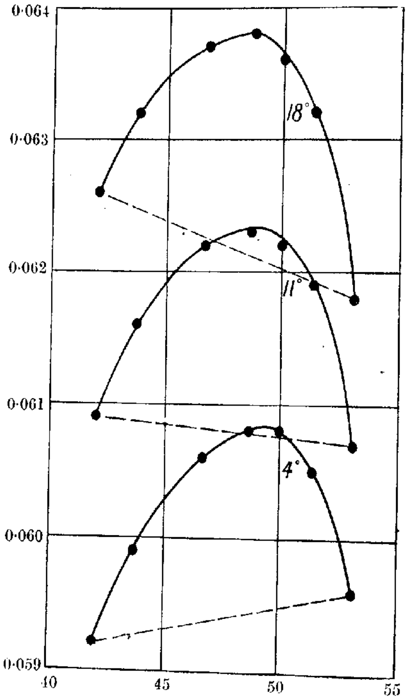
Contraction per c.c. of solution.

$x = P.$
$y = R - 1.$

The position of the minimum is so largely determined by the mere density differences of the two components that it cannot locate precisely the percentage of the combination.

The euthetic point (see Bousfield, *loc. cit.*) is generally very close to the neighbourhood of the point of definite composition. The values of the contraction per c.c. of solution which determine the euthetic point are given in table IV and set out in Fig. 2. The maxima correspond with the euthetic point, and occur:

FIG. 3.



Contraction per gram of solution.

$x = P$.

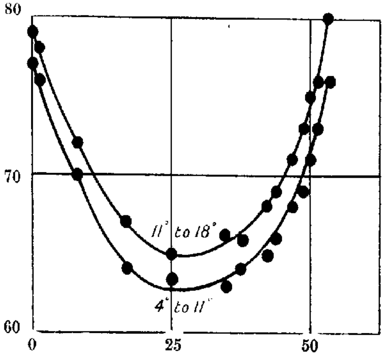
$y = \Delta$.

for 4° at about 49·2 per cent.
for 11° ,, 48·4 ,,
for 18° ,, 47·6 ,,

The actual position of the euthetic point is determined, not only by contraction due to combination, but also by contraction due to changes in the polymerisation of the constituents. The high temperature coefficients for both constituents indicate that these changes are notable. The percentage 49·2 at 4° corresponds very nearly with the composition $3HNO_3,2N_2O_4$.

If we take the curves in Fig. 3, in which the values of the contraction per gram of solution are set out, the effect of polymerisation is to some extent excluded, and the maxima for 4° and 11° appear to occur at 49·3 per cent., whilst that for 18° is again shifted slightly to the left. On the whole, then, it may be said

FIG. 4.



Temperature-coefficients of specific volumes of mixtures of nitric acid and nitrogen peroxide.

$x=P$.
$y=$ Temperature-coefficient α.

that the indications point to the composition of the definite compound $3HNO_3,2N_2O_4$, which corresponds with 49·33 per cent.

An inspection of Fig. 4, in which the temperature coefficients are set out, shows a definite minimum at 26·7 per cent., which appears to be the same for each range of temperature; this corresponds with the definite composition $4HNO_3,N_2O_4$. The first part of the specific volume curve shown in Fig. 1 is approximately straight, which indicates that the whole of the nitrogen peroxide added up to about 15 per cent. enters into this combination with nitric acid. Furthermore, the proportions of nitric acid and the compound, $4HNO_3,N_2O_4$, derived from the mass-action relation give a calculated specific volume which corresponds closely with the actual specific volume curve for a considerable distance, that is, until the effect of the increasing proportion of the still denser combination becomes sensible. On the whole, we may conclude that at least two definite compounds exist in the solutions, namely, $4HNO_3,N_2O_4$ and $3HNO_3,2N_2O_4$.

The Composition of the Double Layers.—The specific volume curves have a gap between about 54 and 92 per cent. If at 4—18° a mixture between these limits is made, the solution separates into two layers, which are mutually saturated.

Nitrogen peroxide is soluble in nitric acid up to about a 54 per cent. solution, but the solubility of nitric acid in nitrogen peroxide is very much less. In order to determine the maximum solubilities at different temperatures, the two components were shaken together from time to time at the required temperatures, forming a cloudy liquid, and kept in a thermostat until the two clear layers were completely separated. The different layers were then drawn off into a pyknometer at the required temperatures, and again kept in the thermostat at these temperatures during the adjustment of the pyknometer. The resulting density determinations enabled the compositions to be determined.

In table V are given the density observations for saturated solutions of nitric acid in nitrogen peroxide, together with the specific volumes at the temperatures and the resulting percentage, p, of nitric acid in the saturated solutions.

TABLE V.

Saturated Solutions of Nitric Acid in Nitrogen Peroxide.

	D.	v.	Percentage of nitric acid.
4°	1·48742	0·67231	4·90
11	1·47351	0·67865	6·67
18	1·45940	0·68521	8·05

Since at this end of the specific volume curves they are practically straight lines, the percentages are easily calculated from the formula

$$v_0 - v_t = \beta p,$$

where v_0 = specific volume of nitrogen peroxide, v_t = specific volume of solution containing p per cent. of nitric acid, the values of the constants being:

	4°.	11°.	18°.
v_0	0·67435	0·68172	0·68938
β	0·000424	0·000476	0·000526

It will be observed that the solubility of nitric acid in nitrogen peroxide rises rapidly with temperature, being about doubled in the range from 0° to 20°. The values indicate that the solubility would vanish at about −10°.

In table VI are given the density observations for saturated solutions of nitrogen peroxide in nitric acid, together with the specific volume at the temperatures and the approximate percentages of nitrogen peroxide in the saturated solutions.

TABLE VI.

Saturated Solutions of Nitrogen Peroxide in Nitric Acid.

	D.	v.	P.
4°	1·65432	0·60448	54·4
11	1·63942	0·60997	54·3
18	1·62501	0·61538	54·0

In this case, the approximate compositions are determined diagrammatically from a large-scale specific volume curve. The temperature of my laboratory in the end of May when these last observations were taken made them very difficult. It is, however, clear that the change of solubility with temperature is in this case very small, and it appears to diminish with rising temperature.

ST. SWITHIN'S,
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[*Received, August 29th,* 1918.]

IV.—*The Effect of Dilution in Electro-titrimetric Analyses.*

By GILBERT ARTHUR FREAK.

THE first application of conductivity measurements to analysis is that due to Küster and Grüters (*Zeitsch. anorg. Chem.*, 1903, **35**, 454), who showed that acids could be titrated accurately by these means. Later, Küster, Grüters, and Geibel (*ibid.*, 1904, **42**, 225) proved the accuracy of the method even when such substances as potassium dichromate and potassium permanganate were present in the acid solution. The estimation of acetic acid in vinegar, of total acid in red wine, of magnesia, and of various alkaloids was also shown to be possible.

Further work has demonstrated that the method is capable of very varied application. Amongst the uses to which it has been put may be noticed the analysis of wines by Duboux (*Chem. Zeit.*, 1913, **37**, 879) and by Duboux and Dutoit (*Compt. rend.*, 1908,

147, 134), the preparation of neutral ammonium citrate solutions by Hall (*J. Ind. Eng. Chem.*, 1911, **3**, 559), and the analysis of soil solutions by Van Suchtelen and Itano (52*nd Ann. Rep. Mich. Board of Agric.*, 1913, 49). The last-named workers have also published (*J. Amer. Chem. Soc.*, 1914, **36**, 1793) the results of experiments on the estimation of chlorides, sulphates, nitrates, phosphates, potassium, calcium, ferrous iron, strong and weak acids, and of chlorides and phosphates in urine. Quite recently, Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) has shown that certain bivalent metals in the form of their sulphates can be determined accurately by the conductivity method by titration with barium hydroxide. Meerburg (*Versl. v. h. Centr. Lab. t. b. h. v. h. Staatsoez. o. d. Volksgehondh.*, 44–54, 1917; *Chem. Weekblad*, 1917, **14**, 1054) has reported adversely on the method as applied to the estimation of sulphates by barium acetate and of calcium by oxalic acid, but mentions that good results may be obtained in the determination of alkalinity in potable waters.

It is noteworthy that, although the method has been applied to so many reactions, no attention has been paid to the lower limit of concentration at which accuracy may still be obtained. Most of the experiments have been carried out on relatively concentrated solutions (seldom weaker than $0{\cdot}1N$), the only reference to results with very dilute solutions being one by Van Suchtelen and Itano (*loc. cit.*), who state that the titration of as little as 5 c.c. of $0{\cdot}001N$-sulphuric acid with $0{\cdot}01N$-sodium hydroxide can be performed accurately. In those titrations involving the precipitation of a salt, the solubility of which would be expected to limit the sensitiveness of the method, this point has not been touched upon.

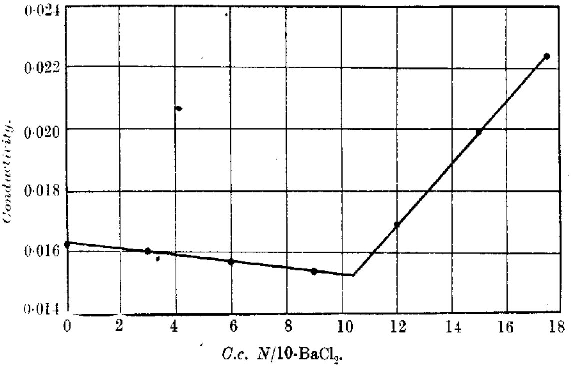
It appears, therefore, to the author that an investigation of this nature was desirable. If the method is capable of yielding accurate results at very low concentrations, many estimations, for example, those carried out in the analysis of potable waters, could be made without previous concentration of the solutions. The present communication is concerned with the limits of the method as applied to the estimation of sulphates, chlorides, calcium, and magnesium. Rigid accuracy was not aimed at, the object being to find to what extent the method could compete with ordinary gravimetric or volumetric processes without the introduction of troublesome precautions. To that end, beyond the use of standardised measuring vessels and of "purest" commercial reagents, no special precautions were taken. No attempt was made to keep the temperature of the solutions constant during the titrations, the duration of which was usually fifteen to twenty minutes.

EXPERIMENTAL.

Except for the use of a double receiver telephone, which proved very convenient in minimising the interference of external noises, the apparatus employed was of the usual nature and therefore calls for no special comment.

The liquid to be titrated was placed in a beaker of such a size that thorough mixing could be effected by giving the vessel a rotatory motion, the stationary electrodes serving as a stirrer. The reagent was delivered from a burette capable of being read to 0·01 c.c. The curves were plotted with conductivity as ordinates and volume of reagent as abscissæ, and in order to eliminate experimental errors at least three, and usually more, readings were taken on each limb of the curve.

FIG. 1.



Estimation of Sulphates.

A stock solution of Merck's purest potassium sulphate was prepared and the SO_4 estimated gravimetrically in duplicate as barium sulphate. From this solution weaker solutions were prepared by dilution. For the titration of these, two solutions of barium chloride, approximately $N/10$ and $N/25$ respectively, were prepared and similarly standardised.

Table I shows that the results are accurate only down to a concentration of about 200 milligrams of SO_4 per litre, a typical curve being shown in Fig. 1. When the concentration of SO_4 is 100 milligrams or less per litre, the precipitation of barium sulphate is so incomplete that the resulting curve changes entirely in character, exhibiting irregularity, but no definite break such as appears in Fig. 1.

Van Suchtelen and Itano (*loc. cit.*) added to their solutions a certain amount of the salt that was to be precipitated with the object of avoiding errors due to solubility. In order to test this procedure, a suspension of fine precipitated barium sulphate in distilled water was added to the sulphate solution in the beaker some little time prior to titration. The results are given in Table II.

TABLE I.

Concentration of SO_4, mg. per litre.	Strength of $BaCl_2$.	SO_4 found. Per cent.
990	*N*/10	100·0, 100·4, 99·4
198	,,	99·2, 99·2, 99·2
99	,,	No end-point.
49·5	N/25	

TABLE II.

Concentration of SO_4, mg. per litre.	Strength of $BaCl_2$.	SO_4 found. Per cent.
99	*N*/10	99·7, 99·7
49·5	*N*/25	99·5, 99·2, 99·6
24·7	,,	End-point indefinite.
9·9	,,	

Reference to table II will show that this method succeeded to a certain extent as, by means of it, good results were obtained down to a concentration of about 50 milligrams of SO_4 per litre. However, it was not effective when only 25 milligrams of SO_4 per litre were present, giving curves with an indefinite end-point of the type shown in Fig. 2. Titration at boiling temperature did not alter the character of this curve. In such cases it is possible, by taking only those points well remote from the curved portion, to arrive at an approximate value for the end-point (see dotted lines). For instance, figures derived in this manner from experiments on solutions containing 25 milligrams of SO_4 per litre were about 5 per cent. in excess of the correct value.

Estimation of Chlorides.

The salt chosen for this purpose was a sample of Merck's purest fused sodium chloride. A stock solution of this, together with the approximately *N*/10- and *N*/25-silver nitrate solutions used for titration, was standardised by duplicate gravimetric estimations as silver chloride.

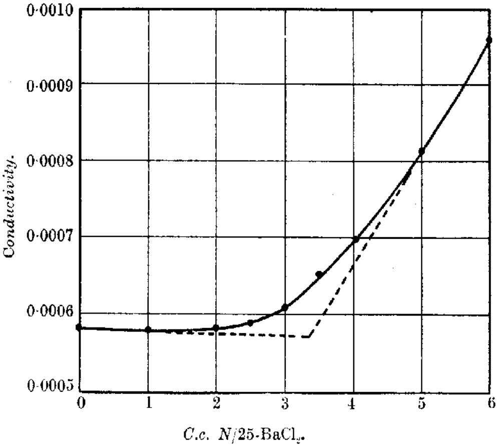
The results obtained with varying concentration of chlorine are shown in table III.

TABLE III.

Concentration of Cl, mg. per litre.	Strength of $AgNO_3$.	Cl found. Per cent.
1000	$N/10$	99·7, 99·3
200	,,	100·1, 99·3, 100·8
50	$N/25$	100·2, 100·9
10	,,	100·6, 100·8
5	,,	End-point indefinite.

As in the case of sulphates, a limit of concentration is reached at which the method fails, the figure in this instance being 10 milligrams of chlorine per litre. The addition of precipitated silver chloride before titration did not render the end-point sharp at lower concentrations.

FIG. 2.



The type of curve obtained in this estimation is similar to that shown in Fig. 1.

Estimation of Calcium.

A stock solution of calcium chloride was prepared by dissolving pure calcite in hydrochloric acid and eliminating the excess of acid by repeated evaporations on the water-bath. Both this solution and the approximately $N/10$-ammonium oxalate solution employed in the titrations were standardised by means of potassium permanganate.

Table IV shows the results obtained.

TABLE IV.

Concentration of Ca, mg. per litre.	Ca found. Per cent.
500	100·0, 100·4, 99·2, 100·4
200	99·1, 100·6, 99·1
100	End-point indefinite.

As in the case of the determination of chlorides, previous addition of the precipitated salt did not lead to sharp end-points at the last-mentioned concentration. In three such experiments, figures given by producing the straight portions of the curves gave 97·0, 97·6, and 95·8 per cent. respectively of the amounts taken.

Estimation of Magnesium.

A solution of Merck's purest magnesium sulphate was employed, standardisation being effected by duplicate estimations as magnesium pyrophosphate. An approximately $N/10$-sodium hydroxide solution, standardised by means of sulphuric acid and pure sodium carbonate, was used for titration.

Variation of the concentration of magnesium gave results shown in table V. The typical curves for these cases have no minimum, but exhibit a definite break.

TABLE V.

Concentration of Mg, mg. per litre.	Mg. found. Per cent.
539	99·2, 99·7, 99·7
269·5	99·7, 100·1, 100·4, 100·1
202	100·8, 99·9, 100·8, 100·6
134·5	End-point indefinite.

Addition of magnesium hydroxide prior to titration lead to no improvement at the last-mentioned concentration.

In connexion with the estimation of magnesium by this method it is interesting to note that Harned (*loc. cit.*) says, "This titration gives only a fairly easily detectable end-point for the change in direction of the plot before and after the end-point is not great. A reagent must, therefore, be sought which will increase the difference in the slopes at the end-point." For this reason he employed barium hydroxide to titrate solutions containing magnesium sulphate. Apart from the fact that the use of this reagent, to be effective, demands that the magnesium shall be present as sulphate and the total elimination of carbon dioxide from the solution, comparison of Harned's figures with those recorded above shows that the use of barium hydroxide does not present any definite advantage. It appears that errors from other sources are of greater magnitude than that derived from difficulty in reading the intersection of the two limbs of the curve.

Summary of Results.

(1) The determination, by means of conductivity measurements, of sulphates, chlorides, calcium, and magnesium has been studied at low concentrations.

(2) It has been shown that, in relatively weak solutions, very small quantities of each of the above mentioned may be estimated, without any attempt at temperature control, with an error not exceeding ±1 per cent.

(3) In each case a limit of dilution is reached at which the results cease to be accurate, smooth conductivity curves being obtained. With the exception of the case of sulphate estimations, saturation of the solution with the salt to be precipitated does not lead to an improvement in this respect.

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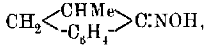
[*Received, August 6th,* 1918.]

V.—*The Optically Active* neo*Methylhydrindamines.*

By (the late) Lt. Joseph Walter Harris.[*]

The reduction of β-methyl-α-hydrindoxime,  $CH_2\left\langle\begin{matrix}CHMe\\C_6H_4\end{matrix}\right\rangle C{:}NOH$, with sodium amalgam and acetic acid leads to the formation of two

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[*] Lt. J. W. Harris, B.Sc., was one of those who, actuated by a high sense of patriotic duty, joined the O.T.C. of the University College, Nottingham, before there was any immediate prospect of a war, and his efficiency and enthusiasm led to his promotion to the rank of colour sergeant. In the summer of 1914 he had just completed his first piece of research work and when war was declared he immediately volunteered for active service. Shortly afterwards he was given a commission in the 3rd Lincolns and went to the Western front, where he was killed in action during the early part of the war.

His death was a great blow to all who knew him, whether in civilian or in military life; he was a most promising chemist, an ideal officer. The present *dl*-bases, one of which may be isolated by the fractional crystallisation of the hydrochlorides prepared from the mixture (Kipping and Clarke, T., 1903, **83**, 913). The other base cannot be obtained, at any rate easily, in this way or by a similar treatment of the normal sulphates, benzoates, cinnamates, or picrates, but by fractionally crystallising the *d*-bromocamphorsulphonates and mechanically separating the obviously different crystals, both the *dl*-bases can be ultimately obtained in a state of purity (Tattersall and Kipping, T., 1903, **83**, 918).

As this method of separation was unsatisfactory, the author of this paper, at the suggestion of Professor Kipping, made some further experiments on the subject, and found that the two *dl*-bases in the crude product could be isolated in the manner described below. He then succeeded in resolving the *dl-neo*-base into its optically active components, both of which were obtained in a state of purity.

All the four optically isomeric β-methylhydrindamines, therefore, have now been characterised; the two *neo*-bases, which form only about 25 per cent. of the original mixture, have very low molecular rotations compared with those of the other two methylhydrindamines.

Separation of Methylhydrindamine and neo*Methylhydrindamine by means of their Hydrogen Oxalates.*

The aqueous solution of the mixed bases obtained by the reduction of methylhydrindoxime was neutralised with finely divided oxalic acid, and a further equal quantity of acid was added. This solution was then concentrated and cooled. The first fraction consisted of tufts of long, silky needles, and was nearly pure methylhydrindamine hydrogen oxalate. Subsequent fractions were similar, but the needles gradually became less well defined, and when about two-thirds of the total substance had been separated the deposits consisted of hard, crystalline masses. The latter, after several recrystallisations from water, yielded tufts of needle-like prisms which were *neo*methylhydrindamine hydrogen oxalate. Some ammonium salts separated in large, transparent masses from time to time, but these were easily removed by extracting the salt of the organic base with alcohol. By the above method about five-sixths of the original mixture was separated into the two *dl*-salts, the pro-

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paper is an account of his work, which he handed to me before he went to the front, and except the few lines of introduction and some immaterial alterations, the matter is given in his own words.—F. S. K.

portion being about three to one, methylhydrindamine being present in the larger quantity.

dl-*Methylhydrindamine hydrogen oxalate*,

$$C_{10}H_{11}\cdot NH_2,C_2H_2O_4,H_2O,$$

crystallises from water, in which it is readily soluble, in tufts of long, silky needles melting at 110—111°. These are hydrated and lose water at 70—80°; at 100° some decomposition is observed, but this is not noticeable in the melting-point tube. The dehydrated salt melts at 143—145° with slight decomposition:

0·4338 lost 0·031 at 80°. $H_2O=7{\cdot}14$.

The above formula requires $H_2O=7{\cdot}06$ per cent.

The benzoyl derivative of the base, made in the usual way, crystallised from alcohol in needles melting at 150°, showing the base to be methylhydrindamine (Tattersall and Kipping, *loc. cit.*).

dl-neo*Methylhydrindamine hydrogen oxalate*,

$$C_{10}H_{11}\cdot NH_2,C_2H_2O_4,2H_2O,$$

in an impure condition, crystallises in compact masses. From water and alcohol the pure compound is obtained in tufts of needle-like prisms, which partly liquefy at about 100° and finally melt at 173—175°, which is the melting point of the anhydrous salt. When treated with benzoyl chloride, the salt gave a benzoyl derivative, crystallising in needles and melting at 169°, which is the melting point of the benzoyl derivative of *neo*methylhydrindamine (Tattersall and Kipping, *loc. cit.*): *

0·4336 lost 0·0568 at 90°. $H_2O=13{\cdot}1$.

The above formula requires a loss of 13·2 per cent.

0·1454 anhydrous salt gave 0·3246 CO_2 and 0·0834 H_2O; $C=60{\cdot}8$; $H=6{\cdot}4$.

$C_{12}H_{15}O_4N$ requires $C=60{\cdot}8$; $H=6{\cdot}33$ per cent.

Resolution of dl-neo*Methylhydrindamine.*

dl-neo*Methylhydrindamine hydrogen oxalate* (20 grams) was decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with tartaric acid, a further equal quantity of the acid being added to form the hydrogen salt. The solution was then concentrated to a small bulk, allowed to cool, and a crystal of pure *l*-*neo*methylhydrindamine hydrogen tartrate introduced. A deposit consisting of tufts of needles separated and was collected. The amount of this fraction was roughly about one-third of the whole. If the solution was allowed to remain too long before it was filtered, the needle-like crystals became covered with white masses. This first fraction was recrystallised from water until its melting point became constant and consisted of *l-neo*methylhydrindamine hydrogen tartrate (about 8 grams). The mother liquors, on further concentration and seeding, gave deposits of white masses, obviously a mixture and melting over a wide range. The last mother liquors gave long, white needles melting at 165°. It was, however, found to be impossible to isolate a pure compound from these mother liquors, owing to the great solubility of the salt.

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* Since the melting point of the *A*-base described by Kipping and Clarke (*loc. cit*) was 169°, it is evident that by the fractional crystallisation of the hydrochlorides of the mixed bases, the salt of *dl-neo*methylhydrindamine is first isolated, whereas in the case of the *d*-bromocamphorsulphonates the salt of *dl*-methylhydrindamine forms the most sparingly soluble fraction.—F. S. K.

The whole of the mother liquor was therefore decomposed with sodium hydroxide, the base distilled in steam, and the distillate neutralised with hydrochloric acid. On concentrating the solution, long needles of *dl-neo*methylhydrindamine separated, but the final mother liquor was found to contain a salt which was more readily soluble in water than that of the *dl*-base, and the solution of this salt showed dextrorotation.

To obtain this dextrorotatory base, the active mother liquor was decomposed with sodium hydroxide, the base distilled in steam, and the solution neutralised with *d*-bromocamphorsulphonic acid. The solution was concentrated until it became turbid and allowed to remain, when a mass of needles separated. These were recrystallised from water until the melting point became constant at 229—230°. This substance was found to be *d-neo*methylhydrindamine *d*-bromocamphorsulphonate.

l-neo*Methylhydrindamine hydrogen tartrate*,

$$C_{10}H_{11}\cdot NH_2,C_4H_6O_6,H_2O,$$

the salt which forms the most sparingly soluble portion described above, crystallises from water or alcohol in large, vitreous prisms, often growing together in leaf-like masses. It is hydrated, and when heated in a melting-point tube it partly liquefies at about 100° and finally melts at 173°. It is readily soluble in water, less so in alcohol, and practically insoluble in ethyl acetate, acetone, benzene, or chloroform:

0·3522 lost 0·0204 at 100°. $H_2O = 5·71$.

The above formula requires $H_2O = 5·71$ per cent.

Samples dried at 100° gave, in a 200 mm. tube in aqueous solution, the following results:

Wt. of salt.	Vol. of solution.	α.	$[\alpha]_D$.	$[M]_D$.
0·7116 gram ………	25 c.c.	0·65°	11·4°	34°
0·4600 " ………	"	0·42	11·4	34

As the molecular rotation of the tartaric acid ion in its metallic hydrogen salts is $[M]_D$ 42°, that of the base is $[M]_D$ $-8°$.

l-neo*Methylhydrindamine* d-*bromocamphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2,C_{10}H_{14}OBr\cdot SO_3H,$$

is moderately soluble in water, and crystallises from the warm solution in aggregates of needles, the solution first becoming milky if the salt is not free from the optically active isomeric base. These needles are hydrated, but lose all their water on exposure to the air. The freshly crystallised substance when heated in a melting-point tube partly liquefies at about 80° and finally melts at 214°. It is more readily soluble in alcohol than in water, and easily dissolves in ethyl acetate, chloroform, or acetone, but is insoluble in ether.

The anhydrous salt was examined in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.	α.	$[\alpha]_D$.	$[M]_D$.
0·5068 ………	25 c.c.	2·32°	57·2°	262°
0·3856 ………	,,	1·75	57·1	261

Taking the molecular rotation of the bromocamphorsulphonic acid ion to be $[M]_D$ 270°, these results give a value of $[M]_D$ $-8°$ or $-9°$ for the base.

l-neo*Methylhydrindamine hydrochloride*, $C_{10}H_{11}\cdot NH_2,HCl$, is much more readily soluble in water than the hydrochloride of the *dl*-base, and crystallises from this solvent in long, silky needles. It is very readily soluble in water or alcohol and also dissolves in ethyl acetate or chloroform, but is practically insoluble in ether or carbon tetrachloride. When heated in a melting-point tube, the substance begins to char at about 235°. The air-dried salt is anhydrous.

The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solution.	α.	$[\alpha]_D$.	$[M]_D$.
0·5250 ……………	25 c.c.	$-0·13°$	$-3·1°$	$-5·7°$
0·7986 ……………	,,	$-0·23$	$-3·6$	$-6·5$
0·7754 ……………	,,	$-0·21$	$-3·4$	$-6·2$

l-neo*Methylhydrindamine* d-*camphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,$$

is very readily soluble in water, and crystallises in long, vitreous prisms. The air-dried salt is anhydrous, and when heated sinters at about 210° and finally melts at 220°. It is readily soluble in chloroform, sparingly so in alcohol or acetone, and practically insoluble in ether or ethyl acetate.

The following results were obtained in aqueous solution in a 200 mm. tube:

Wt. of salt.	Vol. of solvent.	α.	$[\alpha]_D$.	$[M]_D$.
0·5898 ……………	25 c.c.	0·54°	11·4°	43·2°
0·5282 ……………	,,	0·50	11·8	44·7

Taking $[M]_D$ for camphorsulphonic acid as 49°, these results give for the base $[M]_D$ $-5·8°$ and $-4·3°$ respectively.

The *benzoyl* derivative of *l*-*neo*methylhydrindamine crystallises from aqueous alcohol in long, silky needles melting at 171°.

d-neo*Methylhydrindamine* d-*bromocamphorsulphonate*,

$C_{10}H_{11}·NH_2,C_{10}H_{14}OBr·SO_3H$,

is readily obtained in a pure condition from the active base contained in the mother liquors from the *dl*-hydrochloride (see above). It crystallises from warm water in tufts of fine, silky needles, and, as with many other bromocamphorsulphonates, the warm solution becomes milky when the salt separates unless it is free from its optical isomeride. The freshly crystallised salt contains water, probably one molecular proportion, but it was impossible to obtain accurate determinations on this point, since the salt rapidly loses water in the air and the air-dried salt is anhydrous.

1·69 of the salt, roughly dried in the air, lost 0·544 at 100°.
Loss = 3·2, whereas $1H_2O$ requires a loss of 3·1 per cent.

When the freshly crystallised salt is heated in a melting-point tube it partly liquefies at about 100° and finally melts at 229—230°. It is moderately soluble in water, more readily so in alcohol; it is also soluble in acetone or ethyl acetate, but insoluble in carbon tetrachloride or ether.

d-neo*Methylhydrindamine hydrochloride*, $C_{10}H_{11}·NH_2,HCl$, prepared from the pure bromocamphorsulphonate, was dried at 100° and examined polarimetrically in aqueous solution in a 200 mm. tube.

Wt. of salt.	Vol. of solution.	α.	$[\alpha]_D$.	$[M]_D$.
0·5200 …………	25 c.c.	0·13°	3·1°	5·7°
0·4268 …………	,,	0·10	3·0	5·5

d-neo*Methylhydrindamine hydrogen tartrate*,

$C_{10}H_{11}·NH_2,C_4H_6O_6,H_2O$,

is much more readily soluble in water than the hydrogen tartrate of the *l*-base, and crystallises in aggregates of needle-like prisms:

1·2146 air-dried salt lost 0·0726 at 100°. $H_2O = 5·9$.
The above formula requires $H_2O = 5·71$ per cent.

When heated in a melting-point tube the salt sinters at about 90° and finally melts at 166—167°. The following results were obtained with aqueous solutions of the anhydrous salt in a 200 mm. tube:

Wt. of salt.	Vol. of solution.	α.	$[\alpha]_D$.	$[M]_D$.
0·3122	25 c.c.	0·40°	16·0°	47·5°
0·3328	”	0·43	16·2	48·1

Taking the molecular rotation of the tartaric acid ion in its hydrogen salts as $[M]_D$ 42°, these results give $[M]_D$ 5·5° and 6·1° respectively for the base.

d-neo*Methylhydrindamine* d-*camphorsulphonate*,

$$C_{10}H_{11}\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,$$

crystallises from water in felted masses of needles which melt and decompose at 195—205°. The salt is extremely readily soluble in water and readily so in alcohol or chloroform. It is sparingly soluble in ethyl acetate and practically insoluble in ether.

A sample dried at 100° examined in aqueous solution in a 200 mm. tube gave the following result: 0·6176 gram in 25 c.c. of solution gave α 0·73°, $[\alpha]_D$ 14·8°, $[M]_D$ 56·1°. Taking the molecular rotation of the acid ion as 49°, that of the base is $[M]_D$ 7°.

University College,
Nottingham.

[*Received, December* 16*th*, 1918.]

VI.—*Chromatocobaltiammines.*

By Samuel Henry Clifford Briggs.

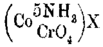
Previous investigations have shown that the chromate radicle possesses considerable residual affinity, and has a strongly marked tendency to form complex salts (Briggs, *Zeitsch. anorg. Chem.*, 1907, **56**, 246; 1909, **63**, 325; Groeger, *ibid.*, 1908, **58**, 412). It was therefore to be expected that the chromatocobaltiammines would be a well-defined and stable class of substances, containing one or more non-ionisable chromate radicles. As soluble compounds containing a non-ionisable chromate radicle have not previously been described, the study of the chromatocobaltiammines was undertaken in order to compare the properties of the chromate radicle in non-ionisable combination with those of the ionisable radicle in the ordinary chromates.

The chromatocobaltiammines are readily prepared by the action of potassium chromate on the corresponding aquo-compounds in solution. Thus, when a solution of potassium chromate is added to a warm solution of an aquopentamminecobaltic salt, a chromatopentamminecobaltic salt (I) crystallises out on cooling. The *nitrate*, *chloride*, and *chromate* of this series were obtained in a pure condition.

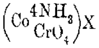
The chromatotetramminecobaltic salts (II) are formed in a similar manner, and the *chromate*, *dichromate*, and *nitrate* were prepared in a pure state. When a solution of a diaquotetramminecobaltic salt is treated with an excess of potassium chromate, *trichromatooctamminedicobalt* (III) crystallises out on keeping. Trichromatooctamminedicobalt is isomeric with chromatotetramminecobaltic chromate (IV), but the two compounds are very different. The former is almost completely insoluble in water, and forms greenish-black crystals containing five molecules of water of crystallisation, whilst the latter is obtained as a greenish-brown precipitate with three molecules of water of crystallisation; it is moderately soluble in water, and its solution gives the reactions of the chromate ion.

Attempts to prepare chromatotriammine compounds by the action of potassium chromate on triaquotriamminecobaltic nitrate were not successful, the product being chromatohydroxotriamminecobalt (V), which, however, was not obtained in a completely pure condition. It therefore appears that when more than two molecules of ammonia in the hexamminecobaltic radicle are replaced by the chromate radicle, the products are unstable in the presence of water, and undergo hydrolysis. This explains why endeavours to prepare potassium cobaltic chromate, $K_3Co(CrO_4)_3$, by oxidising cobaltous salts in the presence of potassium chromate, failed, cobaltic hydroxide and potassium dichromate being obtained. The formation of chromatohydroxotriamminecobalt in the above manner also supports the view that the basic chromates are hydroxo-compounds in accordance with Werner's theory of basic salts ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., pp. 177–178).

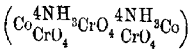
Some evidence was obtained which pointed to the existence of a chromatoaquotriammine series (VI), a compound being prepared which had the composition of chromatoaquotriamminecobaltic dichromate:


$$\left(\mathrm{Co}\begin{matrix}5\mathrm{NH}_3\\ \mathrm{CrO}_4\end{matrix}\right)\mathrm{X}$$

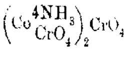
(I.)


$$\left(\mathrm{Co}\begin{matrix}4\mathrm{NH}_3\\ \mathrm{CrO}_4\end{matrix}\right)\mathrm{X}$$

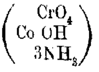
(II.)


$$\left(\mathrm{Co}\begin{matrix}4\mathrm{NH}_3\\ \mathrm{CrO}_4\end{matrix}\mathrm{CrO}_4\begin{matrix}4\mathrm{NH}_3\\ \mathrm{CrO}_4\end{matrix}\mathrm{Co}\right)$$

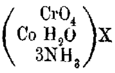
(III.)


$$\left(\mathrm{Co}\begin{matrix}4\mathrm{NH}_3\\ \mathrm{CrO}_4\end{matrix}\right)_2\mathrm{CrO}_4$$

(IV.)

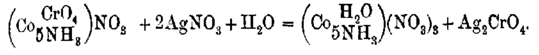

$$\left(\mathrm{Co}\begin{matrix}\mathrm{CrO}_4\\ \mathrm{OH}\\ 3\mathrm{NH}_3\end{matrix}\right)$$

(V.)


$$\left(\mathrm{Co}\begin{matrix}\mathrm{CrO}_4\\ \mathrm{H}_2\mathrm{O}\\ 3\mathrm{NH}_3\end{matrix}\right)\mathrm{X}$$

(VI.)

In the chromatopentammine- and chromatotetrammine-cobaltic salts the chromate radicle in the complex is non-ionisable, no precipitate being obtained when silver nitrate is added to cold, freshly prepared solutions of the pure nitrates. If the mixture is allowed to remain for some time, however, silver chromate is slowly deposited, showing that the chromato-salts have a tendency to pass into the corresponding aquo-salts as seen from the equation:



$$\left(Co\substack{CrO_4\\5NH_3}\right)NO_3 + 2AgNO_3 + H_2O = \left(Co\substack{H_2O\\5NH_3}\right)(NO_3)_3 + Ag_2CrO_4.$$

If the solution is heated the change takes place at once, and silver chromate is immediately precipitated.

The chromate radicle in these compounds reacts with hydrogen ions in the same way as in the ordinary chromates. When an acid is added to a solution of a chromatopentammine or chromatotetrammine salt, the complex is decomposed, as seen from the change in colour of the solution.

In the chromatopentammine salts the chromate radicle fills one co-ordination position according to Werner's theory, whereas in the chromatotetrammine salts it fills two positions.

The entrance of the chromate radicle into the complex is accompanied by marked intensification of colour, and all the chromatocobaltiammines are deeply coloured substances.

EXPERIMENTAL.

Pentammine Series.

Chromatopentamminecobaltic Nitrate, $\left(Co\substack{5NH_3\\CrO_4}\right)NO_3$.—Carbonatopentamminecobaltic nitrate was converted into aquopentamminecobaltic nitrate, and potassium chromate was then added to the solution, the details of the preparation being as follows.

Carbonatopentamminecobaltic nitrate (2·5 grams) was dissolved in 100 c.c. of water, a little dilute nitric acid was added, and the solution was gently warmed to expel carbon dioxide. The liquid was then just neutralised by potassium hydroxide, diluted to 300 c.c., and heated to 60—70°. One and a-half grams of potassium chromate in 100 c.c. of water also heated to 60—70° were added, and the clear solution was allowed to crystallise. The chromatopentamminecobaltic nitrate separated in brownish-red, acicular crystals (2·2 grams), which were collected, washed with a little water, and dried in the air.

Found: $Co = 18{\cdot}51$; $CrO_3 = 31{\cdot}74$; $NH_3 = 26{\cdot}36$.

$\left(Co\substack{5NH_3\\CrO_4}\right)NO_3$ requires $Co = 18{\cdot}35$; $CrO_3 = 31{\cdot}05$; $NH_3 = 26{\cdot}44$ per cent.

The salt was moderately soluble in cold water, and the freshly prepared solution was not precipitated by silver, lead, or barium salts, but precipitation took place at once on heating. The chromate radicle is therefore situated in the complex, as shown by the above formula, and the salt is isomeric with Jörgensen's nitratopentamminecobaltic chromate, $\left(\mathrm{Co}{\genfrac{}{}{0pt}{}{5NH_3}{NO_3}}\right)\mathrm{CrO_4}$ (*J. pr. Chem.*, 1881, [ii], **23**, 245).

Chromatopentamminecobaltic Chloride, $\left(\mathrm{Co}{\genfrac{}{}{0pt}{}{CrO_4}{5NH_3}}\right)\mathrm{Cl}$.—Chloropentamminecobaltic chloride was converted into aquopentamminecobaltic chloride by Werner's method (*Ber.*, 1907, **40**, 4104), and this was treated with potassium chromate.

Twenty-five grams of chloropentamminecobaltic chloride were heated with 625 c.c. of water and 62·5 c.c. of concentrated aqueous ammonia until the chloride was completely dissolved. After cooling, the liquid was just neutralised with hydrochloric acid, and heated to 60°. Sixteen grams of potassium chromate in 500 c.c. of water, also heated to 60°, were then added, and the mixture was allowed to cool. After crystallisation was complete, the salt was collected, washed with a little water, and dried in the air. Twenty-three grams of brownish-red crystals (*A*) were thus obtained. The mother liquor was heated to 50° and 4 grams of potassium chromate dissolved in a little water were added. On cooling, 1·2 grams of a second salt (*B*) were obtained in yellowish-brown prisms, almost insoluble in cold water, but readily soluble on warming to give a yellow solution. The salt *A* was anhydrous, but *B* contained water of crystallisation; otherwise the salts were similar in composition, as seen from the analyses:

A. Found: Co = 19·86; $\mathrm{CrO_3}$ = 33·97, 34·27; Cl = 12·02; $\mathrm{NH_3}$ = 27·30, 27·15, 27·08.

$\left(\mathrm{Co}{\genfrac{}{}{0pt}{}{CrO_4}{5NH_3}}\right)\mathrm{Cl}$ requires Co = 19·96; $\mathrm{CrO_3}$ = 33·83; Cl = 12·00; $\mathrm{NH_3}$ = 28·81 per cent.

B. Found: Co = 16·91; Cl = 9·80; $\mathrm{CrO_3}$ = 29·94; $\mathrm{NH_3}$ = 26·6; $\mathrm{H_2O}$ = 13·95.

$2\left(\mathrm{Co}{\genfrac{}{}{0pt}{}{Cl}{5NH_3}}\right)\mathrm{CrO_4,5H_2O}$ requires Co = 17·31; Cl = 10·41; $\mathrm{CrO_3}$ = 29·36; $\mathrm{NH_3}$ = 25·0; $\mathrm{H_2O}$ = 13·22 per cent.

The solution of the salt *A* on addition of silver nitrate gave a copious precipitate. This was filtered off, and on treatment with dilute nitric acid was found to consist of silver chloride coloured by the presence of a trace of silver chromate. The reddish-yellow filtrate, on heating, deposited a precipitate of silver chromate. The salt *A* was therefore *chromatopentamminecobaltic chloride*, $\left(Co^{CrO_4}_{5NH_3}\right)Cl$.

The solution of the salt *B* on addition of silver nitrate gave a red precipitate, which was filtered off, the filtrate being only faintly coloured. The precipitate consisted of silver chromate. It dissolved in dilute nitric acid, leaving only a trace of silver chloride. The salt *B* was therefore a hydrated *chloropentamminecobaltic chromate*, $2\left(Co^{Cl}_{5NH_3}\right)CrO_4,5H_2O$.

Various preparations of the salt *A* (chromatopentamminecobaltic chloride) were made, but in all cases the ammonia content was low. The salt could not be purified by crystallisation from hot water, as it was then found to contain a little of the corresponding chromate, $\left(Co^{CrO_4}_{5NH_3}\right)_2CrO_4$, which is very sparingly soluble in water. The reason for the low percentage of ammonia could not be ascertained, and this is all the more remarkable as the salt, on treatment with silver chromate, gave the corresponding chromate in a high degree of purity.

Chromatopentamminecobaltic Chromate, $\left(Co^{CrO_4}_{5NH_3}\right)_2CrO_4,3H_2O$.—Two grams of silver nitrate were precipitated in the cold with 1 gram of potassium chromate, and the precipitate was washed two or three times by decantation. The supernatant liquid was separated as far as possible by decantation, and the precipitate was then poured into a solution of 3 grams of chromatopentamminecobaltic chloride in 150 c.c. of water at 60°, the mixture being well shaken. After a few minutes the silver chloride assumed a dense form, and crystallisation began. The silver chloride was then rapidly collected, and the filtrate, which no longer gave the reactions of the chloride ion, was allowed to crystallise. *Chromatopentamminecobaltic chromate* separated in glistening, scaly crystals, similar in colour to silver chromate. The yield was 1·5 grams. The crystals consisted of a trihydrate, which lost $2\frac{3}{4}$ molecules of water after exposure over sulphuric acid in a vacuum for two or three weeks (loss = 7·16. $2\frac{3}{4}H_2O$ require a loss of 7·17 per cent.). The resulting hydrate, $4\left(Co^{CrO_4}_{5NH_3}\right)_2CrO_4,H_2O$, became anhydrous above 100°. The complete analysis of the trihydrate gave:

Found: $Co = 17{\cdot}48$; $CrO_3 = 43{\cdot}64$; $NH_3 = 24{\cdot}83$; $H_2O = 7{\cdot}64$.

$\left(Co^{CrO_4}_{5NH_3}\right)_2CrO_4,3H_2O$ requires $Co = 17{\cdot}09$; $CrO_3 = 43{\cdot}6$; $NH_3 = 24{\cdot}68$; $H_2O = 7{\cdot}83$ per cent.

Tetrammine Series.

Carbonatotetramminecobaltic nitrate was prepared by Jörgensen's method (*Zeitsch. anorg. Chem.*, 1892, **2**, 282), and this was converted into diaquotetramminecobaltic nitrate by acidification of its solution. On treating the solution of diaquotetramminecobaltic nitrate with potassium chromate, either chromatotetramminecobaltic nitrate, chromatotetramminecobaltic chromate, or trichromato-octamminedicobalt could be obtained in the pure state, according to the conditions employed.

Chromatotetramminecobaltic Nitrate, $2\left(Co\substack{CrO_4\\4NH_3}\right)NO_3,H_2O$.—A solution of 4 grams of carbonatotetramminecobaltic nitrate in a little water was treated with dilute nitric acid, warmed gently to expel carbon dioxide, just neutralised with potassium hydroxide, and the volume made up to 40 c.c. Twenty grams of ammonium nitrate were dissolved in the liquid, and a solution of 1·2 grams of potassium chromate in 10 c.c. of water was added, drop by drop, in the cold, with vigorous stirring. The stirring was continued for a minute or two until crystallisation was complete, and the dark reddish-brown deposit was then immediately collected, washed with a little water, and dried in the air. The yield was 0·9 gram. The product was a hemihydrate, which lost its water of crystallisation after exposure for two days over sulphuric acid in a vacuum.

Found: Co = 18·86; CrO_3 = 31·68; NH_3 = 21·34; H_2O = 3·67.

$2\left(Co\substack{CrO_4\\4NH_3}\right)NO_3,H_2O$ requires Co = 18·77; CrO_3 = 31·83; NH_3 = 21·69 H_2O = 2·87 per cent.

The salt was moderately soluble in water, giving a deep brown solution. Silver, barium, or lead salts did not precipitate the freshly prepared, cold solution, but precipitation took place at once on heating. The cold solution was also completely precipitated if allowed to remain for several days after the addition of the reagent, showing that the chromate radicle is gradually eliminated with the formation of a diaquotetrammine salt, for example,

$$\left(Co\substack{CrO_4\\4NH_3}\right)NO_3 + 2AgNO_3 + 2H_2O = \left(Co\substack{2H_2O\\4NH_3}\right)(NO_3)_3 + Ag_2CrO_4.$$

Chromatotetramminecobaltic Chromate, $\left(Co\substack{CrO_4\\4NH_3}\right)_2CrO_4,3H_2O$.—Four grams of carbonatotetramminecobaltic nitrate in 80 c.c. of water were converted into diaquotetramminecobaltic nitrate as described above in the preparation of chromatotetramminecobaltic nitrate. To the cold neutral solution of diaquotetramminecobaltic nitrate thus obtained (100 c.c.) 3 grams of potassium chromate, dissolved in 50 c.c. of water, were added with vigorous stirring. A brown, crystalline precipitate was formed, which was collected immediately, washed with water, and dried with alcohol and ether. The yield was 2·8 grams.

The salt contained three molecules of water as water of crystallisation only, being readily evolved when the substance was exposed in a vacuum over sulphuric acid. The salt was sparingly soluble in water, and its solution was immediately precipitated by silver nitrate, showing that some of the chromate content was ionisable. It follows from these facts and the analyses that the compound must have the formula assigned to it.

Found: $Co=18{\cdot}14$; $CrO_3=45{\cdot}31$; $NH_3=20{\cdot}61$; $H_2O=8{\cdot}26$.

$\left(\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{CrO_4}}{\mathrm{4NH_3}}\right)_2\mathrm{CrO_4,3H_2O}$; $Co=17{\cdot}97$; $CrO_3=45{\cdot}71$; $NH_3=20{\cdot}77$;
$H_2O=8{\cdot}26$ per cent.

Trichromato-octamminedicobalt,

$$\left(\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{CrO_4}}{\mathrm{4NH_3}}-\mathrm{CrO_4}-\genfrac{}{}{0pt}{}{\mathrm{CrO_4}}{\mathrm{4NH_3}}\mathrm{Co}\right),\mathrm{5H_2O}.$$

—Two grams of carbonatotetramminecobaltic nitrate in 30 c.c. of water were converted into diaquotetramminecobaltic nitrate in the manner already described, and the cold neutral solution (50 c.c.) was added, with stirring, to a cold solution of 5 grams of potassium chromate in 50 c.c. of water. The clear liquid deposited a greenish-black, crystalline substance on keeping. This was collected, washed with a little water, and dried in the air.

Found: $Co=17{\cdot}14$; $CrO_3=43{\cdot}32$; $NH_3=19{\cdot}44$; $H_2O=13{\cdot}05$.
$Co_28NH_3(CrO_4)_3,5H_2O$ requires $Co=17{\cdot}04$; $CrO_3=43{\cdot}33$;
$NH_3=19{\cdot}68$; $H_2O=13{\cdot}01$ per cent.

The five molecules of water were readily evolved on exposing the compound in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. In view of the facts ascertained with regard to chromatotetramminecobaltic chromate and described above, it follows that this isomeric compound must be a non-ionisable octamminedicobalt derivative. Its almost complete insolubility in water affords further confirmation of this view. Again, since in the diaquotetramminecobaltic salts the water molecules are in the "*cis*" position (Werner, "Neuere Auschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., p. 347), this trichromato-octamminedicobalt must also have the chromate radicles in the "*cis*" position, and is therefore a 1:1′:2-2′-*trichromato-octamminedicobalt pentahydrate*. Attempts to prepare the corresponding "*trans*" compound by various methods were unsuccessful.

Chromatotetramminecobaltic Dichromate, $\left(\mathrm{Co}^{\mathrm{CrO_4}}_{\mathrm{4NH_3}}\right)_2\mathrm{Cr_2O_7,2H_2O}$.—Four grams of carbonatotetramminecobaltic nitrate were converted into diaquotetramminecobaltic nitrate as described above, and the neutral solution (80 c.c.) was added slowly, with stirring, to a cold solution of 8 grams of potassium dichromate in 80 c.c. of water. The precipitate was immediately collected, washed with a little water, and dried in the air. The yield was 1·9 grams. Three separate preparations were analysed, and the ammonia content was low in every case, for some reason that could not be ascertained.

Found: Co = 15·94; $\mathrm{CrO_3}$ = 53·41, 54·01; $\mathrm{NH_3}$ = 17·48, 16·6, 16·4; $\mathrm{H_2O}$ = 4·98, 4·76, 5·04.

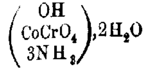
$\left(\mathrm{Co}^{\mathrm{CrO_4}}_{\mathrm{4NH_3}}\right)_2\mathrm{Cr_2O_7,2H_2O}$ requires Co = 15·97; $\mathrm{CrO_3}$ = 54·19; $\mathrm{NH_3}$ = 18·4; $\mathrm{H_2O}$ = 4·88 per cent.

The three molecules of water were readily given off in a vacuum over sulphuric acid, and all were therefore water of crystallisation only. From the proportion of cobalt to chromium (2Co:4Cr) it is evident that the salt is chromatotetramminecobaltic dichromate, $\left(\mathrm{Co}^{\mathrm{CrO_4}}_{\mathrm{4NH_3}}\right)\mathrm{Cr_2O_7}$, and not dichromatotetramminecobaltic chromate, $\left(\mathrm{Co}^{\mathrm{Cr_2O_7}}_{\mathrm{4NH_3}}\right)_2\mathrm{CrO_4}$, in which the proportions are 2Co:5Cr. Consequently the dichromate radicle is ionisable, and the chromate radicle non-ionisable. The salt was moderately soluble in water, and the solution was immediately precipitated by silver and barium salts.

Triammine Series.

Chromatohydroxotriamminecobalt.—Two grams of trinitratotriamminecobalt prepared by Jörgensen's method (*Zeitsch. anorg. Chem.*, 1895, **5**, 185) were dissolved in 40 c.c. of cold water, and the solution was added to a cold solution of 6 grams of potassium chromate in 40 c.c. of water. The brown precipitate (1) was collected, washed with cold water, and dried in the air, when it weighed 1·7 grams. The filtrate, on spontaneous evaporation, deposited crystals of potassium dichromate, as well as of potassium chromate. Two other preparations were made (2 and 3), in which 1 gram of potassium chromate in 10 c.c. of water was mixed with 6·25 c.c. of potassium hydroxide solution (1 c.c. = 0·0448 gram KOH), and the mixture was poured into a solution of 1·5 grams of trinitratotriamminecobalt in 10 c.c. of cold water. The analyses gave:

Found: (1) $H_2O=11{\cdot}5$; $CrO_3=36{\cdot}3$; $Co=22{\cdot}9$; $NH_3=15{\cdot}1$.
(2) $H_2O=11{\cdot}4$; $CrO_3=34{\cdot}5$; $Co=22{\cdot}5$; $NH_3=16{\cdot}8$.
(3) $NH_3=16{\cdot}7$.

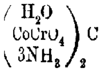


$\left(\begin{matrix}OH\\CoCrO_4\\3NH_3\end{matrix}\right),2H_2O$ requires $H_2O=12{\cdot}9$; $CrO_3=35{\cdot}8$; $Co=21{\cdot}1$; $NH_3=18{\cdot}3$ per cent.

Although impure, the compound was clearly a hydrated chromatohydroxotriamminecobalt.

Chromatoaquotriamminecobaltic Dichromate.—Two grams of trinitratotriamminecobalt in 10 c.c. of cold water were added to a solution of 3 grams of sodium dichromate in 10 c.c. of water, and the mixture was treated with a solution of 0·75 gram of anhydrous sodium chromate in 10 c.c. of water, in the cold. A copious brown precipitate was formed, which was allowed to settle, and then collected, washed with a little water, and dried with alcohol and ether. The product, which weighed 1·4 grams, was only sparingly soluble in cold water. In a vacuum over sulphuric acid, it lost 3 molecules of water after three days, and a further quarter molecule after eighteen days, the weight then remaining constant. The analysis agreed closely with the formula given below.

Found: $3H_2O=7{\cdot}22$; $3\frac{1}{4}H_2O=8{\cdot}16$; $Co=16{\cdot}06$; $CrO_3=54{\cdot}09$; $NH_3=13{\cdot}63$.



$\left(\begin{matrix}H_2O\\CoCrO_4\\3NH_3\end{matrix}\right)_2Cr_2O_7,2H_2O$ requires $3H_2O=7{\cdot}30$; $3\frac{1}{4}H_2O=7{\cdot}91$; $Co=15{\cdot}93$; $CrO_3=54{\cdot}04$; $NH_3=13{\cdot}81$ per cent.

Note on the Preparation of Carbonatopentamminecobaltic Nitrate.

The following method of preparation was found to be more convenient and more economical than that described by Werner and Goslings (*Ber.*, 1903, **36**, 2380).

Twenty grams of cobalt carbonate were dissolved in the smallest ossible quantity of dilute nitric acid and the clear solution 100 c.c.) was poured into a mixture of 250 c.c. of concentrated queous ammonia and 100 grams of powdered ammonium carbonte. Air was drawn through for two or three hours and the soluon was then allowed to remain for twenty-four hours. The mixire was heated for twenty minutes in a porcelain dish on the ater-bath with frequent addition of a small piece of ammonium rbonate. The brown colour of the liquid changed to deep red, nd the mixture was allowed to remain until crystallisation was mplete. After filtration and washing with a little water, the salt was digested with cold water to remove any ammonium carbonate still present. The air-dried product weighed 21 grams. (Found, $Co = 20{\cdot}54$; $NH_3 = 29{\cdot}63$. $\left(Co\begin{matrix}5NH_3\\CO_3\end{matrix}\right)NO_3,H_2O$ requires $Co = 20{\cdot}76$; $NH_3 = 29{\cdot}95$ per cent.) The water was not given off at 100°, or in a vacuum over sulphuric acid at the ordinary temperature.

[*Received, October* 23*rd*, 1918.]

VII.—*Glyceryl Methyl Ether Dinitrate (α-Methylin Dinitrate.)*

By David Trevor Jones.

During recent years, considerable attention has been devoted to the study of the mono- and di-nitrates of glycerol and their chlorides and ethers. The interest in these substances has been stimulated by the technical possibilities which they appeared to offer as ingredients of non-freezing nitroglycerin blasting compositions. Among the substances investigated have been the dinitrate of monochlorohydrin (Kast, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 227), which has been more or less extensively used in such explosives as gelatin astralit, gelatin westfalit, etc. The mono- and di-nitrates of glycerol have been very exhaustively studied by Will (*Ber.*, 1908, **41**, 1107), who commenced the investigation of these substances with the above-mentioned technical object in view. The dimethyl and diethyl ethers of glycerol mononitrate have been described by Paternò and Benelli (*Gazzetta*, 1909, **39**, ii, 312), whilst Vender has described the dinitrates of monoacetin and monoformin (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1907, **2**, 21).

Glyceryl methyl ether dinitrate, which is here described, was prepared by the direct nitration of the α-monomethyl ether of Grün and Bockisch (*Ber.*, 1908, **41**, 3471).

$$OMe{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH + 2HNO_3 \longrightarrow OMe{\cdot}CH_2{\cdot}CH(NO_3){\cdot}CH_2{\cdot}NO_3 + 2H_2O.$$

The product, which was readily isolated, was found to solidify after being well supercooled and stirred. It is a powerful explosive, having about two-thirds the strength of nitroglycerin. It is, however, much less sensitive to shock, although rather more readily exploded by heat. Its effect in lowering the freezing point of nitroglycerin is much the same as that of molecular concentrations of monochlorohydrin dinitrate (Kast, *loc. cit.*) and of ethyl nitrate (Nauckhoff, *Zeitsch. angew. Chem.*, 1905, **18**, 21). All these values, however, are in complete disagreement with the value for the freezing-point constant of nitroglycerin as calculated from a carefully conducted determination of its latent heat of fusion (Hibbert and Fuller, *J. Amer. Chem. Soc.*, 1913, **35**, 979).

The substance did not appear to exist in a second or labile form corresponding with the labile form of nitroglycerin.

EXPERIMENTAL.

Glyceryl α-monomethyl ether was prepared by Grün and Bockisch's method (*loc. cit.*). The product distilled at 120°/18 mm., and the yield was 127 grams, or from 200 grams of monochlorohydrin 66 per cent. of the theoretical. The same yield was obtained on repeating the experiment.

Glyceryl Methyl Ether Dinitrate.

Sixty-three grams of glyceryl α-monomethyl ether were gradually added to 480 grams of a mixture of nitric and sulphuric acids ($HNO_3 = 38{\cdot}6$, $H_2SO_4 = 59{\cdot}0$, $H_2O = 2{\cdot}4$ per cent.), which was cooled in ice-water during the nitration. The initial temperature was 13°. During the operation, the temperature was allowed to rise to 20°, and was maintained at that point until the end. The nitration proceeded quite smoothly, and was easily controlled by regulating the addition of the glyceryl methyl ether. The time occupied by the nitration was from twenty to twenty-five minutes. The product was completely soluble in the mixed acid, and the mixture was slowly poured into 800 c.c. of water, the temperature being allowed to rise to 40°. The bulk of the dinitrate separated, and, after remaining for some little time, the bulk of the aqueous layer was poured off and preserved for extraction. The residue containing the dinitrate was neutralised with a semi-saturated solution of sodium carbonate. The dinitrate was then run off from below, the neutralised aqueous layer being added to the diluted acid which had been previously poured off. The dinitrate was then washed three times at 50° with an equal bulk of 5 per cent. sodium carbonate solution, then three times with water, and was finally dried in a desiccator over calcium chloride. The yield was 75 grams, or 64 per cent. of the theoretical. The neutralised aqueous washings were extracted with ether, and the ethereal solution was washed with 5 per cent. sodium carbonate solution, dried with calcium chloride, filtered, evaporated under diminished pressure, and preserved over calcium chloride in a desiccator. In this way, a further yield of 13·9 grams was obtained, the total yield being thus 88·9 grams, or 77 per cent. of the theoretical.

The dry liquid constituting the first and major portion of the yield was analysed by the combustion method, but on account of its highly explosive nature the weighed-out substance was first converted into a weak dynamite by mixing with excess of previously ignited kieselguhr, the dynamite in turn being mixed with roughly powdered copper oxide and introduced into the combustion tube. The combustion proceeded normally.

The nitrogen was estimated by the nitrometer method, using sulphuric acid, as in the analysis of guncotton:

0·1397 gave 0·1248 CO_2 and 0·0514 H_2O. C=24·36; H=4·03.
0·5492 ,, 132·3 c.c. NO at 16° and 755 mm. N=14·15.
0·638 in 20·45 benzene gave $\Delta t = -0·833°$. M.W.=188.
$C_4H_8O_7N_2$ requires C=24·28; H=4·08; N=14·29 per cent.
M.W.=196.

The substance was therefore undoubtedly α-methylin dinitrate.

Glyceryl methyl ether dinitrate crystallises in white, monoclinic prisms melting at 24°. As first obtained, it was a clear, colourless liquid, which became pale yellow on keeping. It crystallised with difficulty, and remained liquid, even with occasional shaking, for more than two years in a magazine maintained at 15—21°. It distilled at 124°/18 mm., that is, at approximately the same temperature as the glyceryl methyl ether from which it was derived, and some 22° lower than glyceryl dinitrate, the corresponding alcohol.

It is therefore more volatile than nitroglycerin, and when tested at 100° on a watch-glass it was found to volatilise at from seven to eight times as rapidly. The liquid has D_{15}^{15} 1·374 and n_D^{21} 1·4478. It is soluble in benzene, toluene, acetic acid, methyl and ethyl alcohols, chloroform, ether, or acetone, and insoluble in carbon disulphide or light petroleum.

It gelatinises nitro-cotton rapidly at the ordinary temperature, and after warming it yields a gelatin softer and more plastic than that obtained from nitroglycerin.

The chief interest of this substance lies in its explosive properties as compared with those of nitroglycerin. It has about two-thirds the power of nitroglycerin, although it is much less sensitive to shock. Its comparative insensitiveness was demonstrated by submitting to the fall-hammer test unfrozen dynamites each containing three parts of explosive to one part of kieselguhr. Both substances were placed under a steel disk and subjected to the impact of a weight of 1 kilogram, falling from a measured height. The results are set forth in the following table:

Dinitrate.			Nitroglycerin.		
Height of fall. cm.	Detonations.	Failures.	Height of fall. cm.	Detonations.	Failures.
100	2	8	30	10	0
95	1	9	20	10	0
90	1	9	15	9	1
85	0	10	10	0	10

The solid substance was very insensitive. It did not explode even when scratched with the sharp edge of a thin melting-point tube. On the other hand, the dinitrate proved to be more easily exploded when heated than did nitroglycerin. When heated in a glass test-tube in a metal-bath, the temperature being raised at the rate of 5° per minute, it was observed to explode at 182°, the trinitrate exploding at 192°.

Comparative power tests of nitroglycerin and methylin dinitrate dynamites were made with the Trauzl lead block and mortar tests. In the lead block, the dinitrate dynamite gave an expansion of 22·9 c.c., a similar charge of nitroglycerin dynamite giving 30·0 c.c. In the mortar test, the relative powers indicated by the ballistic pendulum were 93·76 kilogram-metres (678 foot-lb.) for the dinitrate dynamite as compared with 124·43 kilogram-metres (900 foot-lb.) for a similar charge of nitroglycerin dynamite. Methylin dinitrate, therefore, would appear to have rather more than two-thirds the strength of nitroglycerin.

In order to determine the lowering effect of the dinitrate on the freezing point of nitroglycerin, a form of apparatus was adopted similar to that used by Kast (*loc. cit.*) for determining the melting points of the nitroglycerin isomerides, and by Hibbert (*Eighth International Congress of Applied Chemistry*, 1912, IV, 37).

About 5 c.c. of the mixture were inserted in a test-tube (15 × 1 cm.) which was fitted into a slightly larger tube, whereby the glyceryl nitrates were protected by an air-jacket from the too rapid action of the freezing mixture. The freezing agent consisted of ice where mixtures of higher melting point were concerned, and of ice and salt for those of lower melting point. The thermometer was allowed to stand in the mixture, direct contact between glass and glass being prevented by enclosing the lower portion of the thermometer bulb in a band of elastic. The stirrer consisted of a flexible piece of platinum wire which was attached to a weighted string wound over a simple pulley, and fastened at the further end to the outer edge of a wooden disk rotated by a motor. The liquid was first supercooled to the extent of about 4° or 5°. It was then inoculated with a small quantity of a frozen mixture of nitroglycerin, wood-pulp, and sodium nitrate, and vigorously stirred. The maximum temperature was then carefully noted and taken as the freezing point. It will be seen that the values found for the molecular depression constant for nitroglycerin vary from 72·4 to 81·0, thus differing not very greatly from those obtained by Nauckhoff (*loc. cit.*) and by Kast (*loc. cit.*) with ethyl nitrate and monochlorohydrin dinitrate respectively. These numbers are in fair agreement with the value 70·5 for the freezing-point constant for nitroglycerin obtained by Nauckhoff (*loc. cit.*) from a determination of its latent heat of fusion. Nauckhoff's method was, however, admittedly defective, and his results differ very considerably from those of Hibbert and Fuller (*loc. cit.*), who found the latent heat of fusion (h) of nitroglycerin at 0° to be 33·2 calories. Corrected to 13°, the melting point of stable nitroglycerin, this would become 33·2 + 13·0 ($c_1 - c_2$), where c_1 and c_2 are the specific heats of solid and liquid nitroglycerin respectively. Accepting Nauckhoff's values of 0·356 and 0·315 for these, the latent heat of fusion of nitroglycerin at 13° would be 33·2 + 13·0 (0·356 − 0·315) = 34·33.

Hence the freezing-point constant

$$\frac{RT^2}{100h} = \frac{0{\cdot}1991 \times (273+13)^2}{100 \times 34{\cdot}33} = 48{\cdot}5.$$

The results are set forth in the following table, which includes Nauckhoff's and Kast's values derived from ethyl nitrate and chlorohydrin dinitrate:

Composition of liquid.			Molecular depression constant.	
Nitro-glycerin. Grams.	Methylin dinitrate. Grams.	Depression of freezing point. (Δ)	Calculated from Δ	Calculated from latent heat (Hibbert and Fuller).
31·69	1·802	2·1°	72·4	48·5
15·31	1·748	4·4	75·6	,,
8·22	1·729	8·7	81·0	,,
	Chloro-hydrin dinitrate.			
21	2·1	4·4	88·4	,,
21	4·2	6·4–7·2	62·7–70·5	
21	6·3	9·4	60·7	
	Ethyl nitrate.		74·1	
			76·0	

Attempts to obtain a labile form of the substance analogous to that of nitroglycerin were made. The liquid was mixed with glass wool and supercooled to varying degrees, with continual stirring with a glass rod. When some of the supercooled liquid which had not been previously frozen was inoculated with a trace of this product, the solid obtained invariably crystallised at 24°.

The author desires to express his indebtedness to Messrs. Nobel's Explosive Co. and to Mr. W. Rintoul, the manager of their Research Section, for the facilities accorded to him for the carrying out and publication of this work.

ARDEER. [*Received, November 7th,* 1918.]

VIII.—*The Inflammation of Mixtures of Ethane and Air in a Closed Vessel: The Effects of Turbulence.*

By RICHARD VERNON WHEELER.

WHEN describing the inflammation of mixtures of methane and air it was noted that the speed at which flame spreads through the mixture in a closed vessel is demonstrably dependent on the degree of mechanical agitation imparted to the mixture, as, indeed, is the speed of flame in all combustible mixtures and under all conditions other than those existing during the propagation of the explosion wave.

This important fact appears first to have been observed, or, at all events, first commented on by Schloësing and de Mondésir about the year 1864. Their experiments, which involved an extended study of the mode of propagation of flame, were carried out mainly with mixtures of carbon monoxide and air, and were undertaken in connexion with a research on the working of gas engines. Mallard and Le Chatelier, to whom the results of the experiments were communicated verbally, have thus described them (*Ann. des Mines*, 1883, [VIII], **4**, 298):

"Ces recherches ont mis en évidence un fait d'une grande importance, l'influence de l'agitation du mélange gazeux sur la vitesse de propagation de la flamme. Des mélanges très lents (et par cette expression nous entendrons ceux dans lesquels la vitesse de propagation est faible) peuvent donner lieu à des propagations pour ainsi dire instantanées, c'est-à-dire à de véritables explosions, quand on provoque au moment de l'inflammation une agitation intérieure très vive, telle que celle que l'on obtient en faisant déboucher au milieu d'une masse gazeuse en repos un jet de gaz animé d'une grande vitesse."

These observations appear to have been overlooked or forgotten until the subject of the agitation or turbulence of gaseous mixtures became of manifest importance during the investigation of gaseous explosions instituted by the British Association for the Advancement of Science. New experiments on the subject, by Dugald Clerk and Hopkinson, are recorded in the Fifth Report of the Committee on Gaseous Explosions (*Rep. Brit. Assoc.*, 1912, 201).

To quote from his Gustave Canet lecture (Junior Institution of Engineers, 1913), Dugald Clerk "had long ago observed that gas engines would have been impracticable had the rates of explosion been the same in actual engine cylinders as in closed-vessel experiments." During his experiments in 1912 he "found that the rate of explosion rise in the same engine varied with the rate of revolution, increasing with increased number of rotations per minute, and was due to the turbulence or eddying caused by the rush of gases into the cylinder during the suction stroke, which persisted during the compression stroke."

By drawing in a charge of mixture into the gas-engine cylinder in the ordinary way, and then tripping the valves and compressing and expanding the charge for one or two revolutions before igniting it, the turbulence was given time to die away. It was found that the effect of thus damping down turbulence was to retard the rate of inflammation of the mixture to a remarkable extent. For example, with a mixture of coal-gas and air containing about 9·7 per cent. of gas, ignition in a gas-engine cylinder under normal conditions at the end of the first compression stroke (the engine being run at 180 revolutions per minute) resulted in the maximum pressure being attained after 0·037 sec.; whilst when ignition was at the end of the third compression stroke, after the charge had been expanded twice and turbulence had subsided, the time taken for the attainment of maximum pressure was 0·092 sec.

Hopkinson experimented on the effects of turbulence at the same time as Dugald Clerk, using a cylindrical vessel 30·5 cm. in diameter and 30·5 cm. long. A small fan was mounted at the centre of the vessel, and comparison was made of the results of igniting similar mixtures with the fan at rest and in motion. With mixtures of coal-gas and air containing 10 per cent. of gas, the times that elapsed between ignition and the attainment of maximum pressure were: (1) with the fan at rest, 0·13 sec.; (2) with the fan running at 2,000 revolutions per min., 0·03 sec.; and (3) with the fan running at 4,500 revolutions per min., 0·02 sec.

Simultaneously with, and independently of, the experiments thus made on behalf of the Gaseous Explosions Committee of the British Association, a problem under investigation for the Explosions in Mines Committee of the Home Office was found to involve a study of the effects of turbulence on the inflammation of gaseous mixtures. The problem was to determine the effect, if any, of the presence of incombustible dusts in suspension on the limits of inflammability of mixtures of firedamp and air. A series of experiments on the ignition of mixtures near the lower limit of inflammability was made with a spherical vessel of about 4 litres capacity (described in T., 1918, **113**, 855) provided with a fan which could be rotated at a high speed so as to agitate the mixture and maintain dust in suspension. Naturally, the fan was rotated whether dust was present or absent, so as to ensure that the comparative experiments required should be made under as far as possible identical conditions. The pronounced effect of turbulence or agitation of a gaseous mixture on the speed at which flame travels through it thus became manifest, for many experiments had previously been made with similar mixtures in the same sphere without the fan.

The fan had four blades, and was attached to a horizontal shaft passing through an air-tight gland near the bottom of the sphere. Each blade extended for 7·5 cm. along the shaft and had a maximum width of 2·5 cm., the edge having a radius of curvature of 9·5 cm. The shaft was so fitted that there was a clearance of 1 cm. between the side of the sphere and the edges of the fan-blades. A slight helical twist was given to each blade.

Several experiments were made with mixtures of ethane and air near the lower-limit of inflammability, which, with ignition at the centre of a closed spherical vessel of glass of 2·5 litres capacity, is 3·10 per cent. ethane. With 3·0 per cent. of ethane flame travels slowly throughout nearly the whole of the (non-turbulent) mixture in such a vessel; and with 2·9 and 2·95 per cent. of ethane flame spreads through about one-third of the mixture (T., 1911, **99**, 2026). It will therefore be realised that even though a mixture may not contain sufficient ethane to ensure continued self-propagation of flame, part of the mixture may be burnt with a consequent development of pressure in a closed vessel.

The earlier experiments with turbulent mixtures were made with the fan running at 100 revolutions per second. The means of ignition was a secondary discharge (from a "10-inch" *X*-ray coil) across a spark-gap of 12 mm. at the centre of the sphere, produced by breaking a current of 10 amperes in the primary circuit of the coil, the trembler being locked. Such a discharge is more than adequate to ignite any inflammable mixture of ethane and air when the mixture is still, yet it was found that no ignition, or, rather, no propagation of flame, took place with a mixture of ethane and air containing as much as 3·2 per cent. of ethane when that mixture was agitated by the fan at 100 revolutions per second. On stopping the fan and allowing the turbulence to subside, ignition took place readily with complete inflammation of the mixture and the development of a pressure of 3·4 atmospheres.

Similarly, with mixtures containing 3·15 and 3·05 per cent. of ethane no ignition could be obtained, whilst the fan was running (at 100 revolutions per second), however frequently the discharge was passed, although when the mixtures were free from turbulence ignition occurred on the first passage of the discharge. Details of these and similar experiments are as follow:

Ethane in mixture. Per cent.	Result.
3·20	No ignition when the fan was running at 100 revolutions per sec. With the fan at 40 revolutions per sec. ignition took place, a pressure of 4·5 atm. being recorded 0·25 sec. after ignition. Without the fan running, a pressure of 3·4 atm. was developed.
3·15	No ignition could be obtained when the fan was running at 100 revolutions per sec. Without the fan, ignition occurred at once, a pressure of 3·2 atm. being recorded.
3·10	With the fan at 40 revolutions per sec. ignition occurred on the fourth passage of the discharge. With the fan at 20 revolutions per sec. ignition occurred at once. A pressure of 4·4 atm. was developed on both occasions, 0·177 sec. after ignition in the first experiment, and 0·287 sec. after ignition in the second.
3·05	No ignition could be obtained when the fan was running at 100 revolutions per sec. Without the fan, ignition occurred at once and a pressure of 2·8 atm. was recorded.
3·00	No ignition with the fan at 100 revolutions per sec. With 20 revolutions per sec. ignition occurred at once and a pressure of 4·3 atm. was recorded 0·30 sec. after ignition.
2·95	With the fan running at 20 revolutions per sec. ignition occurred when the discharge was maintained (the trembler of the coil being in action). A pressure of 4·2 atm. was recorded.

Strong agitation of a mixture poor in combustible gas renders it difficult to ignite, or, to be precise, renders it difficult for the flame that no doubt occurs during the passage of the discharge to spread away therefrom and travel throughout the mixture. This difficulty increases as the degree of agitation is increased and as the percentage of combustible gas is decreased. When, however, the flame in such an agitated mixture does manage to spread away from the source of ignition it travels rapidly.

From the high pressure developed when a mixture was ignited that contained 2·95 per cent. of ethane and to which turbulence had been imparted by a fan running at 20 revolutions per second, it seemed that flame must have travelled through a greater proportion of the mixture than the one-third observed when the mixture was quiescent. An apparatus was therefore devised to enable the appearance of the flames in turbulent mixtures to be examined. The apparatus, which consisted essentially of a globe of glass of about 4 litres capacity, is shown in Fig. 1, and needs no description. Preliminary experiments were made to determine the direction of the air-currents induced by the fan, which had two helical blades and revolved on a vertical axis. From the behaviour of coloured powders introduced into the globe while the fan was spinning it appeared that air was drawn from the centre of the globe towards the axis of the fan, and was discharged at the periphery of the latter as a spiral current directed obliquely * around the walls of the globe.

Mixtures of methane and air were used for the experiments. Normally, the lower-limit for central ignition of methane–air mixtures in a closed sphere is 5·6 per cent. methane; the flame travels upward from the spark at the centre until it occupies one-third of the vessel, when it travels downwards as a horizontal disk to the bottom. The appearance of the flames in mixtures containing less than 5·6 per cent. of methane is shown in Fig. 3, T., 1911, **99**, 2025.

When a 5·6 per cent. mixture of methane and air was agitated by spinning the fan at about 50 revolutions per second, a succession of discharges from an induction coil, the trembler of which was in operation in the usual manner, apparently failed to cause ignition. On close observation, however, it was seen that a pointed tongue of flame appeared at each passage of the discharge directed *downwards* towards the axis of the fan, apparently drawn thither by the current. The flame was about 2 cm. long and formed a sharp-pointed cone having the spark-gap (12 mm. in length) as its base. Occasionally, if the discharge were maintained, a fine filament of flame darted rapidly over a distance of a few cm. towards the fan. The speed of the fan was now reduced to about 30 revolutions per second and a discharge passed across the gap. The sequence of events was too rapid to be followed by the eye. It was observed that a downward-pointing tongue of flame was produced as before, and that this tongue, after some hesitation, shot towards the axis of the fan; the whole vessel then seemed to fill with flame and the glass was shattered into powder.

Further experiments were made with mixtures containing less methane. On two occasions the globe was shattered owing to the rapidity with which the mixture contained in it was inflamed, but in a number of experiments, notably in several with a mixture containing 5·0 per cent. of methane (see T., 1914, **105**, 2595), the movement of the flame could be followed; or, at all events, owing to the persistence of retinal impressions, the course taken by the flame was apparent. An attempt has been made to indicate the appearance of the flame to the eye at a given instant by the shaded additions to Fig. 1. The impression produced can be described as that of a spiral whirlwind of flame, the axis of the spiral being inclined at an angle; in effect, the flame seemed to follow the course of the current induced by the fan. It appeared also that the flame passed several times through the mixture before it finally died away at the centre of the sphere. Analysis of the products of combustion of the 5·0 per cent. mixtures of methane and air showed that all the methane had been burnt.

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* No doubt owing to an unequal setting of the blades of the fan.

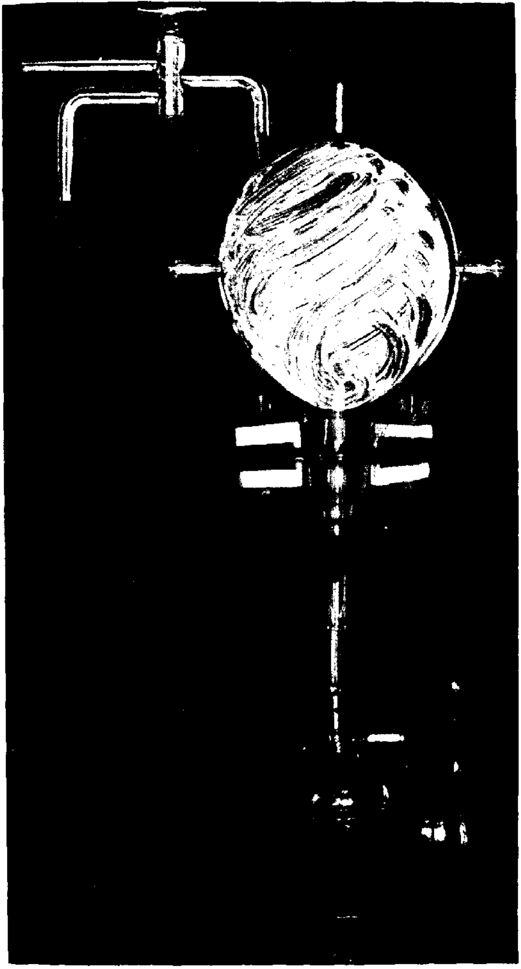
There can be little question, as a result of these observations, that the action of the form of turbulence studied in causing an enhanced speed of combustion of a weak inflammable mixture of methane or ethane and air within a closed vessel is purely mechanical. The flame, which normally would be propagated mainly by conduction of heat from a burning to an unburnt "layer" of mixture, is forcibly dragged in the wake of the rapid current induced by the fan, burning the mixture in its path. The difficulty experienced by the flame in such weak mixtures in travelling away from the source of ignition if the speed of the fan is very great is no doubt due to the fact that mixtures of the paraffins with air exhibit a considerable "time-lag" when the temperature of the source of heat that causes ignition is but little above the ignition-temperature, a condition obtaining with the flames of limit mixtures.

With richer mixtures, in which flame normally spreads at an equal speed in all directions from the source of ignition, the action of turbulence is mechanical also. To quote Mallard and Le Chatelier (*loc. cit.*, p. 350):

"Lorsque le gaz dans lequel progresse la flamme est à l'état d'agitation, la vitesse de propagation augmente parceque la chaleur se transmet non seulement en vertu de la conductibilité du mélange gazeux, mais encore en vert. des différences de vitesse des diverses parties de la masse. La surface de la flamme, au lieu de garder une forme constante et régulière, se deforme à chaque instant, augmente de largeur en multipliant les points d'inflammation et, par suite, en rendant plus rapide la progression de la combustion."

If this explanation is correct, it follows that (1) the greater the turbulence the more rapid should be the combustion; and (2) a

Fig. 1

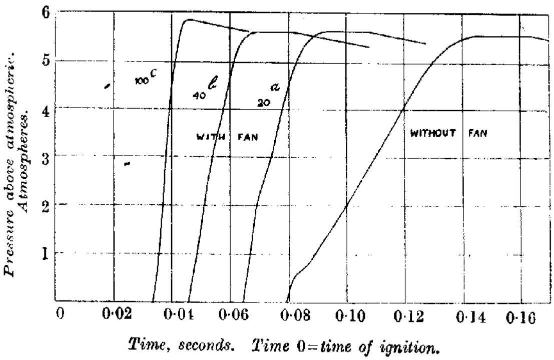


[To face p. 86

mixture in which the speed of flame normally is slow should be more susceptible to the effects of turbulence than one in which the speed of flame normally is rapid.

The first deduction has received experimental verification by Hopkinson, whose results have already been quoted. His results are confirmed by a series of experiments in the 4-litre sphere with mixtures of ethane and air containing 3·85 per cent. of ethane, the time-pressure curves for which are reproduced in Fig. 2. The time-intervals between ignition and the attainment of maximum pressure were: mixture at rest, 0·146 sec.; fan running at (*a*) 20 revs. per sec., 0·091; (*b*) 40 revs. per sec., 0·070 sec.; (*c*) 100 revs. per sec., 0·045 sec. Additional points that should be noted as regards these curves are: (1) the slight increase of pressure obtained with the turbulent mixtures (*a*) and (*b*), and the marked increase with the turbulent mixture (*c*) as compared with that produced by the quiescent mixture; and (2) the disappearance from the curve for turbulent mixture (*c*) of the horizontal portion at maximum pressure noticeable in the other three curves. An explanation of these effects is offered later.

Fig. 2.



In order to test the second deduction that should follow if the explanation suggested for the action of turbulence is correct, two series of experiments were made with mixtures of ethane and air ranging between the lower-limit mixture and that giving the maximum pressure on combustion. In the one series the fan was run at a constant speed of 100 revolutions per second; in the other the fan was at rest. The time–pressure curves for typical experiments of these two series are shown in Figs. 3 and 4,* the curves for the

FIG. 3.

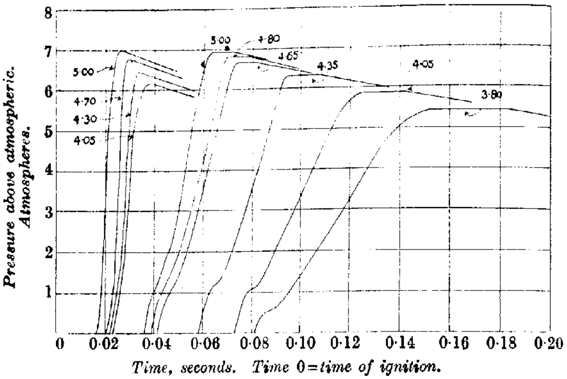
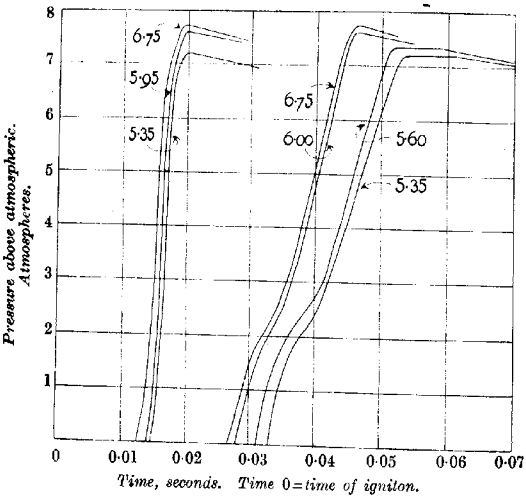


FIG. 4.



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* It should be noted that the unit of time employed in plotting the curves in Fig. 3 (and Fig. 2) is double that in Fig. 4. This contraction of the time-scale is rendered necessary from considerations of space.

turbulent mixtures occupying the left-hand portion of each diagram.

From these curves the time that elapsed between ignition and the attainment of maximum pressure for each mixture can be determined. These times, together with the times for mixtures not included in Figs. 3 and 4, are recorded in the table that follows:

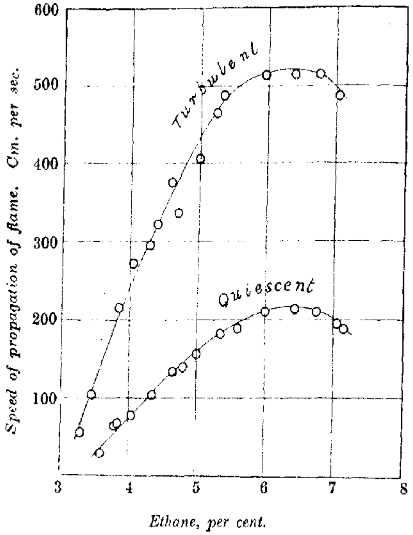
Ethane in mixture. Per cent.	Time between ignition and the attainment of maximum pressure. Seconds.	
	Without turbulence.	With turbulence.
3·30	—	0·176
3·45	—	0·096
3·60	0·332	—
3·80	0·152	—
3·85	0·146	0·045
4·05	0·124	0·036
4·30	—	0·033
4·35	0·094	—
4·60	—	0·026
4·65	0·073	—
4·70	—	0·029
4·80	0·070	—
5·00	0·063	0·024
5·25	—	0·021
5·35	0·054	0·020
5·60	0·052	—
5·95	—	0·019
6·00	0·0465	—
6·40	—	0·019
6·45	0·046	—
6·75	0·0465	0·019
7·05	0·050	0·020
7·15	0·052	—

It has been shown (T., 1918, **113**, 852) that these time-intervals can be used to calculate, for each mixture, the mean speed of propagation of flame between the centre and the top of the sphere, a distance of 9·75 cm. The speeds thus calculated are shown plotted against percentages of ethane in Fig. 5. Allowing for the irregularities, which are naturally more noticeable with the turbulent than with the quiescent mixtures, the speeds for equivalent percentages of ethane in the two sets of experiments, as deduced from the smoothed curves, are given in the table on p. 90.

The conclusion that a mixture in which normally the speed of flame is slow should be affected by turbulence to a greater extent than one in which normally the speed of flame is rapid is thus proved experimentally by the gradual diminution in the value of the ratio B/A.

The Development of Pressure.—On referring to the time–pressure curves for mixtures without turbulence given in Figs. 3 and 4, and

FIG. 5.



comparing them with the curves for mixtures of methane and air previously published (*loc. cit.*, Fig. 2, p. 847), it will be seen that both sets of curves are of the same type. All the mixtures of

Mean Speed of Propagation of Flame from Centre to Top of Sphere. Cm. per sec.

Ethane in mixture. Per cent.	Without turbulence. (*A*).	With turbulence. (*B*).	Ratio *B*/*A*.
3·6	35	142	4·06
3·8	55	195	3·54
4·0	75	237	3·17
4·2	95	284	2·99
4·4	112	320	2·85
4·6	129	360	2·79
4·8	144	400	2·77
5·0	158	430	2·72
5·2	172	462	2·68
5·4	185	485	2·62
5·6	195	500	2·56
5·8	202	510	2·52
6·0	210	518	2·47
6·5	212	518	2·44
6·7	200	495	2·47

ethane and air up to and including that containing 5·6 per cent. of ethane have time–pressure curves which exhibit the three stages of development noticeable with the mixtures of methane and air. The explanation of these stages offered when describing the methane curves can be applied also in the present instance.

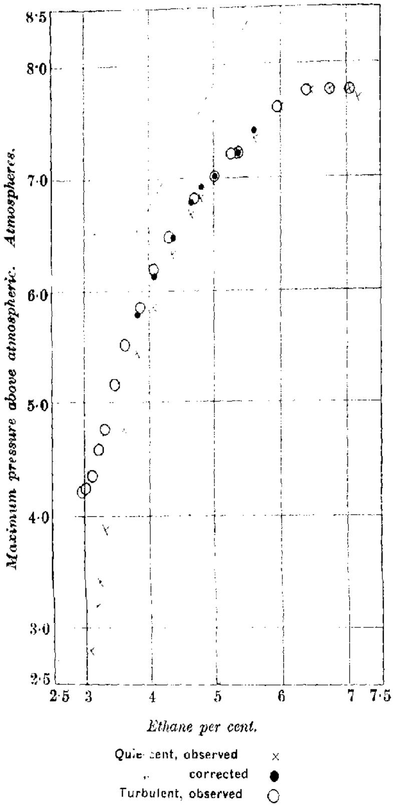
Support is given to the assumption then made that the second stage of development, during which the recorded pressure remains constant, represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. For it will be found that a graphical "correction" applied, in conformity with this assumption, in the manner described (*loc. cit.*, p. 849) yields results for the maximum pressures in close agreement with the maxima recorded by equivalent mixtures when turbulent, over the whole range from 3·80 per cent. ethane (at and above which percentage the flame travels from the centre in all directions at the same speed) upwards.

This is best shown in Fig. 6, where the observed maximum pressures for all the mixtures experimented with, both turbulent and quiescent, and the "corrected" maxima for the latter, are shown plotted against percentages of ethane. It should be observed that the magnitude of the correction, as is to be expected, diminishes in proportion as the speed of inflammation of the mixture increases. Similarly, the magnitude of the difference between the maximum pressures recorded with like mixtures when turbulent and quiescent also decreases as the speed of inflammation of the latter increases, until with mixtures containing more than 5·6 per cent. of ethane no difference is observable between the two sets of pressures. Further, the crests of the time–pressure curves for the quiescent mixtures that contain more than 5·6 per cent. of ethane no longer remain horizontal over a measurable length of time, but the cooling curves begin as soon as the maxima are attained.

Pier (*Zeitsch. Elektrochem.*, 1909, **15**, 536), who used the pressures developed by the inflammation of different mixtures in a closed vessel to determine the specific heats of various gases, has made observations which have a bearing on the question of the effects of turbulence.

Using a manometer of similar construction to the Petavel gauge (*Phil. Mag.*, 1902, [vi], **3**, 461), Pier found exact agreement between the observed and the calculated pressures produced by mixtures the combustion-temperatures of which exceeded 1600°. For this reason he combatted Nagel's opinion ("Versuche über Zundgeschwindigheit explosibler Gasgemische," *Mitteilungen über Forschungsarbeiten des Ingenieurwesens*, Vol. 54, 1908) that with central ignition in a spherical vessel the mixture near the walls must be raised in temperature by adiabatic compression before flame reaches it

FIG. 6.



(an opinion that had already received experimental verification by Hopkinson), and suggested that the interchange of heat between different portions of the mixture within the vessel must be practically instantaneous.

This result Pier supposed would be effected by a rapid whirling and mixing of the contents of a spherical vessel owing to a sudden increase of pressure on ignition at the centre. It is clear, if only by reason of the difference observable in the character of the time–pressure curves for ethane–air mixtures with and without artificially-produced turbulence, that Pier's contention cannot be correct; and Hopkinson's measurements of the temperatures within a closed cylindrical vessel at the moment of maximum pressure produced by the inflammation of a mixture of coal-gas and air (*Proc. Roy. Soc.*, 1906, [*A*], 77, 387) should have convinced Pier of its falsity.

In the absence of knowledge regarding the composition of the products of combustion at the moment of attainment of maximum pressure when the ethane–air mixtures contain excess of ethane, it is not possible to calculate the theoretical pressures that should be given by such mixtures on ignition in a closed sphere were there no loss of heat during the propagation of flame. Calculation can, however, be made for those mixtures in which the combustion of ethane can be presumed to be complete. The mixture of ethane with air in which ethane and oxygen are in the theoretical proportions for complete combustion to form carbon dioxide and steam contains 5·63 per cent. of ethane. The dotted line in Fig. 6 represents the calculated maximum pressures over the range 3·8—5·5 per cent. ethane.* It will be seen that a loss of heat of between 9 and 12 per cent., presumably due to radiation during the propagation of flame, is indicated.

A matter for further study is the fact that the mixtures of ethane and air which produce the highest pressures are not those within close range of the mixture containing ethane and oxygen in theoretical proportions for complete combustion (5·63 per cent. of ethane), but lie over a considerably higher range, namely, 6·5—7·0 per cent. The time taken for the attainment of maximum pressure reaches a minimum over the same range, or, in other words, the speed of propagation of flame under the conditions of the experiments is fastest in mixtures containing between 6·5 and 7·0 per cent. of ethane. In this respect the results obtained with mixtures of ethane and air differ markedly from those with methane and air.

Further comparison of these results with those obtained with mixtures of methane and air is reserved for a future communication, which will include the results of similar experiments with other members of the paraffin series of hydrocarbons.

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* The calculations were made in the manner described in T., 1918, **113**, 858, using Langen's values for the specific heats of the gases.

EXPERIMENTAL.

The apparatus used (4-litre sphere) and general method of procedure for the experiments has already been described (*loc. cit.*, p. 854). The ehane was prepared by the action of water on zinc ethyl and was purified by liquefaction by liquid air; the ratio C/A on explosion analysis was 1·25, showing that it contained no impurity.

The majority of the experiments described in this paper were carried out during the year 1912, with the assistance of Mr. M. J. Burgess.

[*Received, November* 15*th*, 1918.]

IX.—*The Ignition of Explosive Gases by Electric Sparks.*[*]

By JOHN DAVID MORGAN.

SOME time ago an investigation was carried out by Dr. R. V. Wheeler and Prof. W. M. Thornton on the ignition of explosive gases by sparks produced in signal bell circuits (Home Office Report on Electric Signalling with Bare Wires, R. V. Wheeler and W. M. Thornton, June, 1916). They used iron-core coils, in conjunction with mechanical means for breaking the circuit Commenting on the results obtained, they state:

"It may be said that ignition by a rapid break flash at a low circuit voltage depends on the inductance voltage at which the flash is formed, and the igniting power of the flash is proportional to the product Li (where L is the inductance of the circuit and i the current prior to breaking the circuit). When the break of the circuit is made slowly, the igniting power of the flash has been found to depend upon its energy, $\frac{1}{2}Li^2$. There are thus two limiting conditions for the igniting power of the flash; at the one the inductance voltage is of importance, at the other the energy. For any given gaseous mixture there is a range of rapidity of break over which the two types of ignition blend, so that under certain conditions the igniting power of the flash may be proportional neither directly to i nor to i^2, but to some intermediate value of it."

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[*] Published with the permission of the Advisory Council for Scientific and Industrial Research.

Then, referring to a previous report (Home Office Report on Battery Bell Signalling Systems, R. V. Wheeler, January, 1915), they cite a case in which it was found that the igniting power of the break flash could be expressed by the relationship $Li^{1\cdot4}=$ constant.

The figures by Wheeler and Thornton in support of the conclusion that Li is constant are given in table I.

TABLE I.

Inductance (L). Henries.	Igniting current (i) at 25 volts. Ampere.	Li.
0·27	0·82	0·220
0·47	0·45	0·212
0·70	0·26	0·182
0·90	0·20	0·180
1·04	0·17	0·177
1·18	0·155	0·183
1·27	0·145	0·184
1·31	0·13	0·170
1·60	0·11	0·176
2·00	0·09	0·180

In the same report they give the number of layers of wire on the magnets used by them, together with the igniting currents. These are given in table II. I have added a third column giving the product N^2i^2, where N = number of layers. As the layers each have the same number of convolutions, N is proportional to the turns. It will be noticed that it can also be said that N^2i^2 is constant, a quantity which has not the same physical significance as Li. The expressions are only comparable when each contains either of the terms i or i^2.

TABLE II.

Layers of wire on magnet (N).	Igniting current (i).	N^2i^2.
4	0·82	10·8
8	0·45	12·8
12	0·26	9·7
16	0·20	10·0
18	0·17	9·3
20	0·155	9·6
22	0·145	10·0
24	0·13	9·7
28	0·11	9·6
32	0·09	8·4

In the earlier report by Dr. Wheeler, a table is given from ich the number of layers on the magnet coil can be deduced, and *the igniting current is added. Using these figures, I have calculated* N^2i^2, and the figures are given in table III.

TABLE III.

Number of layers (N).	Igniting current (i).	N^2i^2.
20	0·17	11·6
16	0·23	13·6
12	0·33	15·6
8	0·55	19·2
6	0·95	32·5

The figures in the third column show that in this case the product N^2i^2 is by no means constant, but progressively increases.

When the flux produced by the current is linked with the whole of the windings, the product N^2i^2 is proportional to the electrokinetic energy of the system so long as the permeability is constant. When the linkage is imperfect or the permeability varies, the energy is not proportional to N^2i^2. From the results above referred to, it is found that when a low tension igniting spark is defined in terms of the coil constants (N or L) and the current (i) prior to the spark, the energy required to produce a spark that will ignite a gas mixture of given composition appears to be constant in some cases and not constant in others.

Experiments with low tension sparks have led me to suspect that such results as those above mentioned, though apparently diverse, have some constant factor in common, and that the disparities are due to the manner in which the results are expressed. There is not implied by this remark any suspicion of the accuracy of the work done by Wheeler and Thornton. They were concerned mainly with determining what circuit conditions could give rise to dangerous sparks, and from that point of view the results were expressed in terms of practical utility. The question raised is as to whether the results as expressed can be employed to determine the property of the spark on which ignition depends.

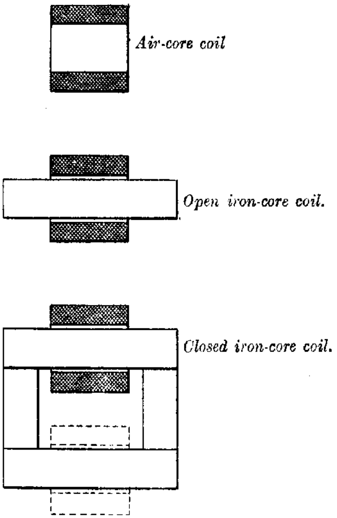
I therefore decided to make a new investigation with low tension sparks, and arrange the experiments to cover a wide range of different magnetic conditions. Six short air-core coils were made according to the particulars given in table IV.

TABLE IV.

No.	Number of turns.	Number of layers.
1	100	2
2	200	4
3	300	6
4	400	8
5	500	10
6	700	14

Two iron cores of relatively large cross-section were also made, one a laminated bar and the other a closed laminated frame, for use with the same coils. The experiments were divided into three groups, which were distinguished only by the differences in the magnetic conditions of the cores. Diagrammatic representations of the coils are shown in Fig. 1. Current was obtained from a 12-volt accumulator. The circuit was completed by a variable resistance of negligible inductance, an ammeter, and a 'flick' contact breaker, the latter being enclosed in the explosion chamber. The contact breaker consisted of a flexible steel prong capable of being rotated into contact with a fixed steel stem, and then flicked over the stem. A coal gas and air mixture of constant composition was used throughout the investigation.

Fig. 1.



The least currents required to produce ignition are given in table V.

TABLE V.

Air-core Coils.

No. of layers (N).	Current (i) amperes.	N^2i^2.
2	4·5	81
4	2·05	67·4
6	1·24	54
8	0·83	44
10	0·575	33
14	0·35	24

Open Iron-core Coils.

No. of layers (N).	Current (i) amperes.	N^2i^2.
2	1·05	4·4
4	0·51	4·3
6	0·35	4·4
8	0·26	4·3
10	0·21	4·4
14	0·15	4·4

Closed Iron-core Coils.

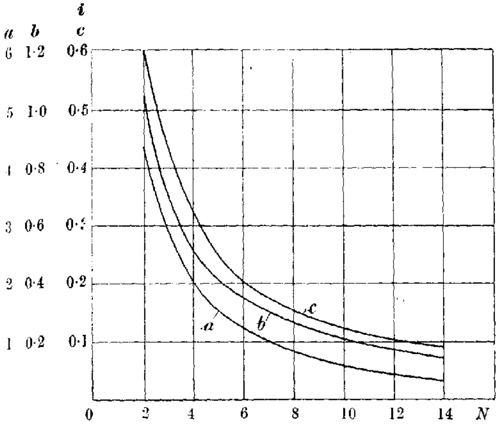
No. of layers (N).	Current (i) ampere.	N^2i^2.
2	0·63	1·6
4	0·32	1·64
6	0·2	1·44
8	0·16	1·64
10	0·13	1·69
14	0·09	1·6

Figs. 2 and 2*a* give the results graphically.

It will be noticed that the product N^2i^2 is not constant for the air-core coils, although it tends to a constant value at the upper value of N, and is constant with the open iron and closed iron-core coils, although the value of N^2i^2 is different in the latter two cases. In other words, the results may be said to be similar in kind to those obtained in Wheeler and Thornton's investigations.

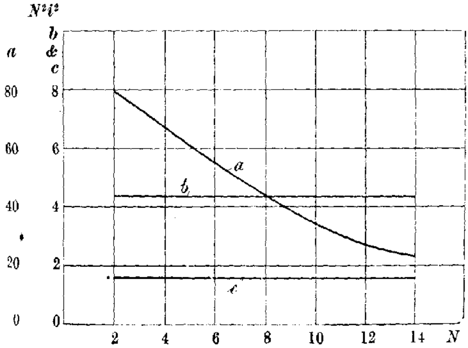
The present investigation differs from those as recorded in the cited reports of Wheeler and Thornton, in that I have carried out measurements on the circuits after interruption. The first step consisted in the use of an arrangement as shown in Fig. 3. This is a Wheatstone bridge in conjunction with a ballistic galvanometer. The inductance coil *a*, non-inductive balance resistance *b*, ammeter *c*, flick contact breaker *d*, variable non-inductive resistance *e*, and battery *f* are all (excepting *b*) as used in the explosion experiments. *a* and *b* are shunted by non-inductive resistances *r* of sufficiently low resistance to eliminate sparking at *d* when the circuit is broken Using with each coil the current values required o give the igniting sparks, the observed "kicks" were plotted gainst N. These are given in Fig. 4. The straight lines indicate that for each group the energy associated with the system prior to interruption was constant, but they give no information as to

FIG. 2.



a = air-core coil.
b = open iron-core coil.
c = closed iron-core coil.

FIG. 2a.



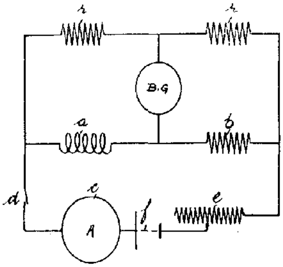
a = air-core coil.
b = open iron-core coil.
c = closed iron-core coil.

whether the energy was the same for each group. The inductances were therefore measured, and found to give $\frac{1}{2}Li^2$ = constant for each group, but different for different groups. As nothing is gained by quoting all the values of all the inductances, only the largest for each group is recorded in table VI.

TABLE VI.

	L.	$\frac{1}{2}Li^2$.
Air-core coil, 14 layer	0·01	0·0006 joule.
Open iron-core coil, 14 layer	0·07	0·0008 „
Closed iron-core coil, 14 layer	0·56	0·0023 „

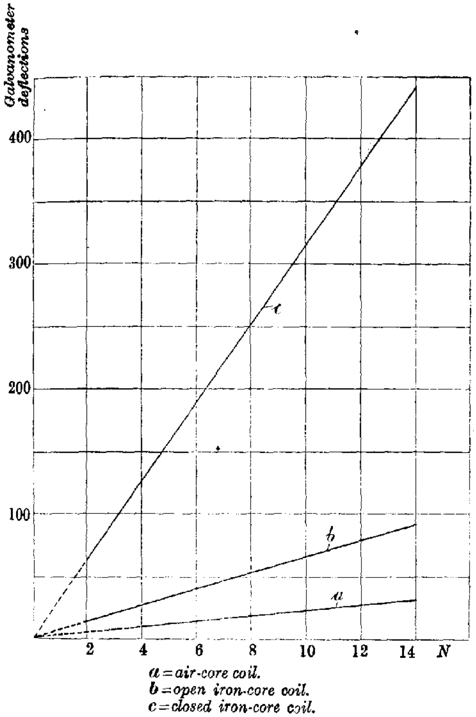
FIG. 3.



It is clearly not permissible to conclude that the energy projected into the sparks in the explosion experiments is constant for a constant magnetic condition, but different when that condition is changed, until it is proved that the differences found are not accounted for by core or other losses. A further step, involving direct spark measurements, was therefore necessary. After trying various schemes, the apparatus shown diagrammatically in Fig. 5 was adopted. *a* is the flick contact breaker used in the explosion experiments. This is enclosed in an ebonite chamber, *b*, to which a capillary tube is sealed. Two things appeared at first to render this device useless. The heat developed by the current passing through the contact breaker when closed was sufficient to interfere with proper measurement of the heating effect of the spark produced on opening the contact breaker. Further, it was difficult to maintain a perfectly gas-tight joint around the rotatable stem carrying the prong of the contact breaker. These troubles were avoided by permitting a slight leak in the chamber and observing (through a microscope) only the "kick" given to the liquid thread in the capillary tube. Using he coils and current values employed in the explosion experinents, it was found that the "kicks" were the same throughout. t follows that the sparks obtained in the three widely varying roups of experiments were identical as regards their impulsive hermal effects.

I do not think it can be argued from the above that the spark

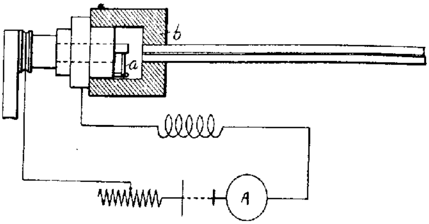
FIG. 4.



ergy was the same in all cases, although this possibility is not cluded.

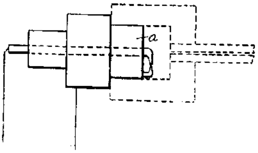
The final step consisted in an attempt to determine definitely hether the energies of the different sparks were the same or not. or this purpose, a high tension winding of fine wire and many rns was placed on one of the limbs of the closed iron core, as shown in dotted lines, Fig. 1, and connected to a small, permanent gap in a spark plug, *a*, Fig. 6. The sparks produced were very small, and several had to be produced in succession to give a deflection definitely readable through the microscope. In place of the flick contact breaker in the primary circuit, a cam-operated interrupter, such as is used in ignition apparatus for internal-combustion engines, was employed. With this interrupter, twelve

Fig. 5.



sparks were obtained from each complete rotation of the cam. The chamber was made perfectly gas-tight, and the deflections were different in character from those of the previous experiment in that they were relatively slow. Taking each of the coils in turn and using the current values obtained in the explosion experiments, the deflections obtained after one complete rotation of the cam were observed. In all cases they were found to be the same.

Fig. 6.



It follows that the total heating effect of the same number of sparks from each coil was the same; consequently, the sparks were of equal energy. Seeing that the sparks in all three groups of experiments gave the same impulsive thermal effects and the sparks in one group gave the same energy effects, it is permissible to argue that the energies of all the sparks in the three groups were the same.

The conclusion of the investigation is therefore that over the wide range of different conditions examined, the igniting sparks had this in common—that they all liberated the same amount of heat energy, a result which is not evident from measurements on the spark circuit prior to the production of the sparks.

Regarding single spark ignition of explosive gases initially at atmospheric temperature and pressure, the main results of investigations which have been published in recent years, and which can be regarded as well established, appear to be as follows:

(1) With a low tension spark, the least spark energy required to ignite a given gas mixture diminishes with increase of the voltage impressed on the spark circuit prior to the production of the spark (The least energy required to start a gaseous explosion, W. M. Thornton, *Phil. Mag.*, 1914, [vi], **28**, 734).

(2) When the circuit voltage is constant, the spark energy required for ignition of a given gas mixture by a low tension spark is constant (see above).

(3) With a high tension spark (which consists of a capacity component preceding an inductance component), the incendivity of the spark (or ability to cause ignition) can be increased by increasing the proportion of energy in the initial part of the spark without increasing the total energy of the spark ("Spark Ignition," J. D. Morgan, *Engineering*, November 3rd, 1916).

(4) The incendivity of a condenser or capacity spark is greater than that of an inductance spark dissipating the same amount of energy (Thornton, *loc. cit.*).

(5) With a capacity spark, the least energy required for ignition of a given gas mixture diminishes as the spark voltage increases (Thornton, *loc. cit.*).

These results clearly establish the fact that the incendivity of a spark does not depend on the total energy of the spark.

It is generally supposed that the energy required to produce ignition of a given inflammable gas mixture is constant for similar physical conditions. If the assumption is correct, then the fact that the total energy of the least igniting spark is found experimentally to vary with the conditions under which the spark is produced suggests that not all of the spark energy is utilised in the process of ignition, but only a portion at the commencement of the spark. It is, of course, possible that the inflammability of a gas as determined by the least energy required to produce ignition is not constant for identical physical conditions of the gas, but it would appear to be useless to attempt an investigation of this point by spark measurements having regard to the facts above mentioned. It is important to note that a spark is a varying source of heat which very rapidly reaches its maximum intensity and then less rapidly disappears. Experiments prove that increase of the initial intensity of a spark results in increased incendivity. As already stated, this suggests that ignition is due only to the initial part of the spark, and that in every spark there is a certain amount of unused energy which makes no contribution to the process of ignition. The proportion of unused energy must diminish as the initial intensity increases, but at present any measurements of the effective portion of the spark appear to be impossible. It follows from this suggested theory of unused energy that any attempts to specify the inflammability of a gas in terms of the total energy of the least igniting spark must necessarily yield the diverse results which have hitherto been obtained.

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X.—*The Physical Constants of Nicotine. Part I. Specific Rotatory Power of Nicotine in Aqueous Solution.*

By HARRY JEPHCOTT.

NICOTINE has been purified and its constants have been recorded by Landolt ("Optical Rotation of Organic Substances"), Nasini and Pezzolato (*Zeitsch. physikal. Chem.*, 1893, **12**, 501), Gennari (*ibid.*, 1896, **19**, 130), Hein (*Diss.*, Berlin, 1896), Přibram and Glücksmann (*Monatsh.*, 1897, **18**, 303), Ratz (*ibid.*, 1905, **26**, 1241), and Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 563). All, with the exception of Ratz, relied on the distillation in hydrogen of anhydrous nicotine. Ratz utilised two methods, namely, fractional distillation in a vacuum and the formation of nicotine zinc chloride followed by distillation. Their results for the specific rotation, which show considerable variation, are as follows:

	$[\alpha]^{20}_{D}$.	D^{20}_{4}.
Landolt	161·55	1·01101
Nasini and Pezzolato	161·29	—
Gennari	162·84	1·01071
Hein	164·18	1·01049
Přibram and Glücksmann	164·91	1·0095
Ratz (by fractional distillation)	166·77	—
,, (from double salt)	169·0 to 169·54	1·00925
Winther	163·85	—

It appeared probable that the variation was due to the presence of the alkaloids nicoteine, nicotelline, and nicotimine, which occur with nicotine, and it was decided to purify nicotine by the method utilised by Pictet and Rotschy (*Ber.*, 1901, **34**, 696) when isolating these alkaloids. Nicotine which had been prepared from tobacco by steam distillation was dissolved in a slight excess of hydrochloric acid and treated with sodium nitrite at low temperature. The nicotine was subsequently liberated by alkali, dehydrated, and fractionally distilled under diminished pressure. Considerable loss of nicotine occurred owing to the formation of oxidation products during the treatment with nitrite.

A quantity, about 2500 grams in all, of commercial nicotine was also converted into nicotine zinc chloride, twice recrystallised, and the nicotine liberated, dehydrated, and fractionally distilled under diminished pressure in a manner similar to that of Ratz (*loc. cit.*).

The distillation was a source of much trouble. In the cold, nicotine readily forms highly-coloured oxidation products on exposure to the air. When hot, this oxidation is extremely rapid, and water is also absorbed. At the temperature of distillation, the vapour readily attacks cork or rubber used for connexions. Well-fitting ground-glass joints are essential, but there proved to be no necessity to flood the apparatus with hydrogen if a sufficiently high vacuum were maintained (20—40 mm. pressure).

The nicotine prepared in this way was colourless and almost without odour in the cold. When kept in bottles filled to the stopper and away from the light, nicotine remains colourless, only the slightest yellow tint being noticed after six months and no change in rotatory power (compare Přibram, *loc. cit.*, p. 303).

For pure nicotine, the density and rotatory power were found to be as follows:

	D_{4}^{20}.	$[\alpha]_{D}^{20}$.
Purified through nitroso-compound	1·00920	168·52
Purified through double chloride (1) ...	1·00925	168·61
„ „ „ „ (2) ...	1·00925	168·40
„ „ „ „ (3) ...	1·00925	168·66

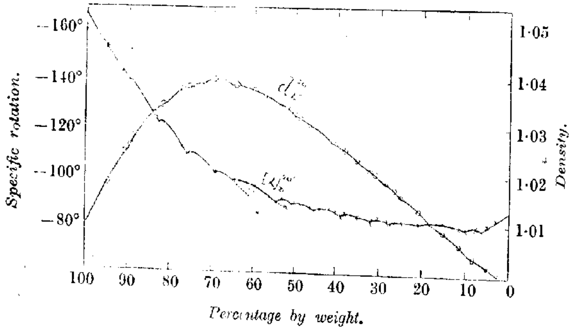
The three sets of figures for the double chloride method refer to three separate and distinct preparations of pure nicotine in that way.

Many dilutions of this nicotine with water were prepared, and the specific gravity and specific rotatory power for them observed. The rotations were measured with a Schmidt and Haensch half-shade polarimeter, using a tube having a length of 100·04 mm.

Percentage by weight.	Grams in 100 c.c.	D_4^{20}.	$[\alpha]_D^{20}$.	Percentage by weight.	Grams in 100 c.c.	D_4^{20}.	$[\alpha]_D^{20}$.
100	100·925	1·00925	168·61	44·004	45·296	1·02936	86·47
95·068	96·801	1·01823	153·06	41·718	42·882	1·02790	86·71
91·084	93·323	1·02458	141·65	40·237	41·308	1·02661	85·09
89·471	91·781	1·02583	138·73	38·798	39·804	1·02592	83·79
88·338	90·820	1·02810	134·11	38·065	39·025	1·02522	85·21
83·336	86·132	1·03356	123·21	37·986	38·950	1·02538	84·98
81·842	84·632	1·03439	121·48	35·098	35·920	1·02341	83·52
77·006	79·921	1·03784	111·47	34·877	35·696	1·02351	83·39
75·538	78·551	1·03836	108·39	32·141	32·810	1·02107	81·83
84·868	77·764	1·03839	108·69	30·973	31·607	1·02048	82·48
69·202	71·963	1·03990	100·47	30·637	31·253	1·02010	82·67
67·538	70·231	1·03988	—	30·291	30·915	1·02060	82·60
64·423	66·918	1·03890	97·82	28·151	28·664	1·01820	81·95
63·950	66·440	1·03894	95·63	26·473	26·930	1·01725	81·78
60·773	63·110	1·03846	94·02	24·975	25·369	1·01588	81·67
59·898	62·131	1·03728	93·69	20·963	21·235	1·01300	80·64
59·649	61·895	1·03765	95·12	20·726	20·995	1·01299	80·06
56·241	58·250	1·03614	91·27	15·023	15·156	1·00880	80·99
54·289	56·245	1·03603	89·27	12·963	13·027	1·00492	79·79
53·096	54·934	1·03463	90·12	11·508	11·579	1·00611	79·43
51·969	53·750	1·03428	86·91	10·012	10·061	1·00611	78·66
50·134	51·777	1·03278	89·03	9·921	9·971	1·00494	79·20
48·949	50·513	1·03194	88·19	7·417	7·441	1·00317	79·94
46·632	48·062	1·03065	86·23	6·604	6·622	1·00276	79·25
46·183	47·629	1·03131	—	4·998	5·006	1·00153	80·48
46·015	47·412	1·03037	86·79	2·505	2·504	0·99970	83·15

The effect of temperature on the density and rotatory power both of pure nicotine and certain of its aqueous solutions has also been observed. For this purpose, a jacketed polarimeter tube was

Nicotine in aqueous solution.



employed, a Sprengel tube being used for the densities. It was not convenient in every case to observe both density and angle at the same temperature, and the density at the temperature at which the rotatory power was observed was obtained from a graph constructed from the recorded densities.

Pure Nicotine.

Temperature.	20°.	21·1°.	40°.	60°.	80°.	97·7°.
D_4^{20} …………	1·00925	1·00865	0·99424	0·97799	0·96184	0·94534

Temperature.	D_4^t (from graph).	$[\alpha]_D^t$.
20°	1·00925	168·20°
29·5	1·0017	168·71
41·5	0·9924	169·09
52	0·9840	169·51
62	0·9760	169·74
69·6	0·9699	169·94
86·4	0·9567	169·73
92·0	0·9521	169·71

Owing to the so-called closed curve of solubility of nicotine in water, it is not possible to observe the rotatory power and density of solutions containing between 7 and 87 per cent. of nicotine at all temperatures up to 100°, since separation occurs at about 60°. Two solutions were therefore prepared which would fall outside this closed curve, and contained 6·638 per cent. and 88·338 per cent. of nicotine. For these, the following figures were found:

Temperature.	Percentage by weight.	Grams in 100 c.c.	D_4^t.	$[\alpha]_D^t$.
20° ……………	6·638	6·682	1·00275	76·82
85 ……………	6·638	6·4188	0·96328	95·29
20 ……………	88·338	90·820	1·02810	134·16
90 ……………	88·338	86·936	0·98412	150·34

It will be observed that the change in rotatory power is marked. On cooling to 20°, the 6 per cent. solution at once showed its original rotatory power, but the 88 per cent. solution did not revert to its former value for some days, although an immediate fall to about $[\alpha]_D^{20}$ 138·0 took place. Difficulty occurs in determining the rotatory power of pure nicotine and its more concentrated solutions, since, owing presumably to light absorption, it is necessary to match a greyish-pink against a grey when taking polarimetric readings. In the case of the more concentrated aqueous solutions, the difficulty is greatly increased owing to the very marked changes in density. In observing the angle of the 88 per cent. solution at 90°, even with a rapid stream of water circulating round the jacket, the change in density by cooling at the exposed surface of the end plates was so marked as to make it almost impossible to get light to pass through the tube, and the rotation recorded must be considered liable to an error of 1°. No such difficulties were experienced with the 6 per cent. solution.

The graphs for density and specific rotatory power of nicotine in aqueous solution both exhibit a series of maxima, and these agree with molecular proportions of nicotine and water. This indication of the formation of a series of hydrates is confirmed by an examination of the freezing points of nicotine solutions.

Between 40 and 80 per cent., the time taken for hydrate-formation is appreciable, and the abnormal points marked were found in cases of solutions when the rotation was observed immediately after mixing. A solution containing 69·2 per cent. of nicotine showed no change in rotation after keeping for twelve months.

The "Closed Curve of Solubility" for Nicotine.

The formation of hydrates of nicotine and their decomposition at higher temperatures shows the true nature of the "closed curve of solubility." Nicotine is only sparingly soluble in water, and water is only sparingly soluble in nicotine, but hydrates of nicotine are miscible with either, a state of balance existing at any given temperature between nicotine, its hydrates, and water.

When the temperature rises, the hydrate-formation reverses, and on the concentration of free nicotine becoming greater than the solubility of nicotine in water at that temperature, separation occurs. By choosing concentrations of nicotine and water such that the limit of solubility of the one in the other was not exceeded, it was possible, as shown above, to note the marked rise in rotatory power as the concentration of free nicotine increased with the rise in temperature, and it is to be expected that with convenience for observing the angle at a sufficiently high temperature, the true rotatory power of nicotine in water would be obtained.

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